

**PHENOLIC-FORMALDEHYDE RESIN COATED METAL SURFACES
AND PROCESS THEREOF**

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Inventor(s): EHARA RYOJI (JP); YOSHIDA MASAYUKI (JP)
Applicant(s):: EHARA RYOJI (JP); YOSHIDA MASAYUKI (JP); HENKEL CORP (US)
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Abstract

Coated metal bearing a coating on its surface that comprises pheno-, naphthol-, or bisphenol-formaldehyde resin comprising specific structural units, has a thickness from 5 to 5000 nm, contains from 5 to 500 mg of carbon atoms present in the resin per m² of surface coated, and covers at least 90 % of the surface of the metal, can be subjected to film lamination onto the coating to provide a composite that has an excellent formability, excellent corrosion resistance, excellent adherence between the laminated film and the metal, and excellent environmental safety.

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(Concise explanations in relevancy)

Japanese laid-open patent publication No. H 10-46101

Laid-open on February 17, 1998

Title of the invention : Phenolic-formaldehyde Resin Coated Metal Surfaces and Process Thereof

Conventional methods of metal surface treatments with the phenolic compound polymer are disclosed in Japanese laid-open patent publication No. 10-46101. This conventional method is not available to form the anti-corrosion coating film on the surface of the lead terminal of the film-sealed non-aqueous electrolyte battery.

Japanese laid-open patent publications No. 10-46101 discloses that titanium fluorine compound is mixed into a treating liquid containing phenol polymer and phosphate compound to prepare a treatment liquid which is then used for carrying out a surface treatment of the lead terminal. In order to improve the adhesion reliability between the lead terminal and the sealant polymer resin film, it is preferable that the anti-corrosion film contains phosphate compound. It is more preferable that anti-corrosion film contains both phosphate compound and titanium fluorine compound for the following reasons.

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| (21) International Application Number: PCT/US97/13685 (22) International Filing Date: 31 July 1997 (31.07.97) (30) Priority Data: 8/219282 1 August 1996 (01.08.96) JP (71) Applicant (for all designated States except US): HENKEL CORPORATION [US/US]; Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): YOSHIDA, Masayuki [JP/JP]; 20-4, Nakao cho Asahi-ku, Yokohama-shi 241 (JP). EHARA, Ryoji [JP/JP]; 624, Shinomiya Hiratsuka-shi, Kanagawa-ken 254 (JP). (74) Agent: WISDOM, Norvell, E., Jr; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US). | | (81) Designated States: AU, BR, CA, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> |
| (54) Title: PHENOLIC-FORMALDEHYDE RESIN COATED METAL SURFACES AND PROCESS THEREOF (57) Abstract Coated metal bearing a coating on its surface that comprises pheno-, naphtol-, or bisphenol-formaldehyde resin comprising specific structural units, has a thickness from 5 to 5000 nm, contains from 5 to 500 mg of carbon atoms present in the resin per m ² of surface coated, and covers at least 90 % of the surface of the metal, can be subjected to film lamination onto the coating to provide a composite that has an excellent formability, excellent corrosion resistance, excellent adherence between the laminated film and the metal, and excellent environmental safety. | | |

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PHENOLIC-FORMALDEHYDE RESIN COATED METAL SURFACES AND PROCESS THEREOF

Field of the Invention

This invention relates to metal that is intended to be laminated to a film, the surface of said metal having a base coating that improves the adherence between the film and the metal surface and improves the corrosion resistance of the laminated metal.

5 The invention also relates to methods for the preparation of this coated metal. More particularly, this invention relates to metal bearing a base coating for film lamination thereon, wherein the base coating imparts an excellent corrosion resistance to the film-laminated metal and products formed therefrom and also provides a sufficiently high film adherence that the film will not debond even when the film-laminated metal is subjected
10 to severe working operations such as drawing, draw-ironing, stretch-drawing, or the like.

Description of the Prior Art

Metals such as iron, steel, aluminum, and so forth are widely used in large amounts in applications such as household electrical appliances and beverage cans, e.g., beer cans. In these applications the metal is first subjected to any of a variety of
15 forming operations and is then painted.

Painting generally uses a solvent-borne or waterborne paint and usually is followed by a baking step. The overall painting operation is associated with a number of emissions: wastes (e.g., waste solvent, etc.) originating with the paint are discharged as industrial wastes; organic compounds (e.g., solvent and low-molecular-weight compounds) driven off during baking and offgases (mainly carbon dioxide) are discharged
20 into the atmosphere. Among the efforts that have recently been undertaken in order to reduce industrial wastes and offgases and maintain the global environment, film-lamination technology has received attention as a replacement for painting.

A large number of inventions have already appeared on can fabrication using film
25 lamination and in related fields. For example, Japanese Granted Patent No. 1,571,783 ("Method for the fabrication of drawn-and-ironed can") concerns the draw-ironing of a polyethylene film-coated mild steel sheet. Japanese Granted Patent No. 1,711,723 ("Draw-ironed can") describes can fabrication from stock bonded with a thermoplastic polyester coating having a prescribed orientation. Japanese Patent Application Laid
30 Open [Kokai or Unexamined] Number Hei 2-263523 [263,523/1990] ("Method for the fabrication of thinned deep-drawn can") concerns coating with a crystalline thermoplastic resin followed by a particular working operation. Japanese Patent Publication [Kokoku] Number Hei 7-57385 [57,385/1995] ("Method for the fabrication of coated, deep-drawn

can") teaches the use of metal sheet coated with thermoplastic resin in the form of polyester film whose main component is ethylene terephthalate. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 3-133523 [133,523/1991] ("Method for the fabrication of thinned drawn can") teaches strong thinning using a laminated metal sheet composed of metal sheet and a coating layer of a particular thermoplastic resin. Japanese Granted Patent No. 1,670,957 ("Draw-ironed can") teaches (i) providing a thermoplastic polyester coating layer and an inorganic oxide layer at the innermost surface and a plating layer of extensible metal at the outer surface wherein the plating layer is composed of specific amounts of at least one selection from a tin layer, nickel layer, and aluminum layer, and (ii) executing a thinning operation to provide a specific overall ironing ratio.

In other examples, Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 4-91825 [91,825/1992] ("Method for the fabrication of coated, thinned can") teaches a method that achieves an economical thinning in deep-drawn cans and generates a very strong and durable protective layer from the coating material. This is achieved by (i) using a laminated metal stock carrying an organic coating of orientable thermoplastic resin film devised to undergo an increase in crystallinity and orientation during re-drawing and (ii) carrying out working under particular drawing conditions including the use of lubricating oil. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 6-218465 [218,465/1994] ("Deep-drawn can and method for the fabrication thereof") teaches coating steel sheet with a tin-containing metal at a coverage ratio of 20 to 80 %; then coating with chromium metal and hydrated chromium oxide; and converting the resulting can stock into deep-drawn cans. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 4-224936 [224,936/1992] ("Resin-coated metal sheet for thinned deep-drawn can with an excellent resistance to denting") teaches the formation on one or both surfaces of a metal sheet of a resin layer of polyester with a particular intrinsic viscosity. This technology provides the excellent processability and in-process corrosion resistance required of metal sheet for thinned deep-drawn cans and in particular imparts denting resistance (resistance to accidental impacts) to the formed can barrel.

Additional examples include Japanese Patent Publication [Kokoku] Number Hei 7-108706 [108,706/1995] ("Fabrication of thinned drawn can"), which teaches the thinning draw-forming of a structure afforded by coating organic resin on surface-treated steel sheet whose substrate is cold-rolled steel sheet that satisfies several specific conditions. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 5-

255864 [255,864/1993] ("Deep-drawn can and method for fabricating same") teaches the fabrication of highly corrosion-resistant deep-drawn cans by coating tin-containing metal under specific conditions on steel sheet and then successively coating the entire surface thereof with chromium metal and hydrated chromium oxide and with organic resin in the order given. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 6-226915 [226,915/1994] ("Polycarbonate-coated metal sheet and method for preparing same") concerns optimization for thinned deep-drawn cans by coating metal sheet with a composite resin layer whose upper ply is polycarbonate resin and whose lower ply is polyester resin. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 6-255022 [255,022/1994] ("Resin-coated metal sheet and method for the preparation thereof") concerns a technology for obtaining an excellent resistance to cold impact working. This is achieved by coating the surface of metal sheet with a resin layer consisting of a blend of polycarbonate and polyester in specific proportions. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 6-155660 [155,660/1994] ("Polyester-coated metal sheet with excellent hot-water resistance") relates to a technology that equips can stock with the necessary excellent processability and corrosion resistance and that prevents opacification of the can exterior even by retort treatment. This is achieved by setting up a specific crystallization ratio and specific residual biaxial orientation (prior to retort treatment) in a polyester layer adjacent to the metal sheet.

Another example is Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 7-138786 [138,786/1995] ("Laminated steel sheet and precursor sheet therefor"). This reference teaches that the corrosion resistance and post-processing film adherence of steel sheet coated with a thermoplastic resin film can be improved by formation in a specific configuration of chromium and tin plating layers and a hydrated chromium oxide layer on the front and rear surfaces of steel sheet. Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 6-238818 [238,818/1994] ("Coated metal sheet can stock and seamless can formed therefrom") teaches a technology for effectively suppressing foaming over, when a carbonated beverage is opened. In this technology, a biaxial molecular orientation is imparted to the surface of polyester film on the inner can surface with the average height, at three points, for the large projections measured when a coarse region is selected in the visual field in an atomic force microscope being specified. In Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 7-178485 [178,485/1995] ("Two-piece can with excellent impact resistance"), improved impact resistance and improved corrosion resist-

ance are obtained by specifying the intrinsic viscosity, degree of axial orientation, and degree of planar orientation of an oriented crystal-containing polyester resin that is the main component of the organic resin.

The substrates for bonding in these references are an inorganic oxide layer
5 formed by chromate treatment, chromate/phosphate treatment, or electrolytic chromate treatment (Japanese Granted Patent No. 1,670,957); chromium metal and hydrated chromium oxide (Japanese Patent Application Laid Open Number Hei 6-218,465); electrolytic chromate-treated steel sheet, precoated tin-free steel (hereinafter usually abbreviated as "TFS"), hydrated chromium oxide coating, composite plating, or alloy
10 plating (Japanese Patent Application Laid Open Number Hei 4-224,936); a hydrated chromium oxide coating at 3 to 30 milligrams of coating per square meter of surface coated (hereinafter usually abbreviated as "mg/m²") as chromium (Japanese Patent Application Laid Open Number Hei 6-226,915); and tin-plated steel sheet or precoated TFS (Japanese Patent Application Laid Open Number Hei 7-138,786). Thus, the bond-
15 ing substrates in these references can be classified into tin plate coatings and chromium-based coatings. However, tin is expensive, and toxic hexavalent chromium is used in the treatments that give the chromium-based coatings.

Paintless can fabrication systems have in fact been realized in practice through the application of the inventions in the references given above. These systems involve
20 the lamination of precoated TFS with polyester film followed by stretch-drawing to fabricate the can. This technology omits the heretofore used painting processes (painting and baking) by substituting the laminated film for the paint film.

This technology has received a great deal of attention as a new approach to beverage can fabrication. At the present time, however, this technology exclusively employs TFS on which a chromium-based coating treatment has been executed, because
25 neither a laminating film nor a laminating method has been developed that can meet the twin demands of high film adherence to the can stock (necessary due to the severe working that occurs after film lamination) and post-processing corrosion resistance (necessary to prevent corrosion by the various contents later put into the cans). As noted
30 above, toxic hexavalent chromium is used in this coating treatment, with the result that the appearance of a chromium-free treatment and coating is strongly desired.

Problems to Be Solved by the Invention

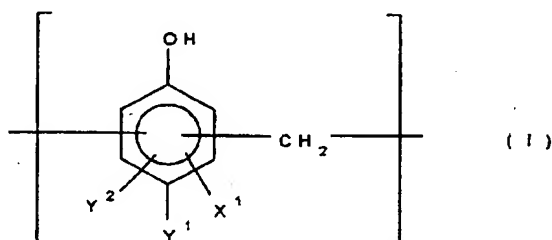
The present invention seeks to solve the problems described above for the prior art. In more specific terms, an object of the present invention is to provide metal stock
35 bearing a chromium-free base coating for film lamination thereon wherein the film-lamin-

at d metal exhibits an excellent adherence by the laminated film and excellent corrosion resistance even after it has been subjected to severe working operations such as, for example, drawing, draw-ironing, and stretch-drawing. An additional object of the present invention is to provide methods for fabricating this coated metal stock.

5 Summary of the Invention

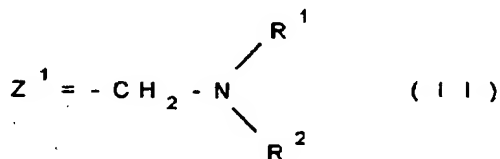
It has been discovered that the objects listed above could be realized by a coated metal whose surface is coated with a special polymer at a particular coating thickness, a particular coating weight, and a particular coverage ratio.

In specific terms, the present invention relates to coated metal bearing a coating
 10 on its surface for film lamination thereto, wherein: the thickness of the coating is from 5 to 500 nanometers (hereinafter usually abbreviated as "nm"); the total mass per unit area of carbon atoms in the coating is from 5 to 500 mg/m²; the coating covers at least 90 % of the surface of the metal, when measured as described below; and the coating comprises, preferably consists essentially of, or more preferably consists of, (optionally
 15 with other specific materials as specified further below) polymer molecules that comprise, preferably consist essentially of, or more preferably, except for end groups, consist of, structural units conforming to general formula (I):



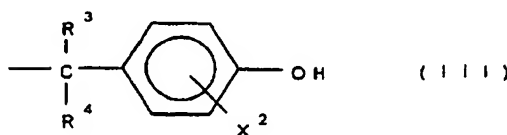
15 in which:

X¹ in each structural unit is a hydrogen atom or a moiety Z¹ conforming to general formula (II):

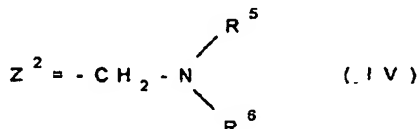


in which each of R¹ and R² is a hydrogen atom, a C₁ to C₁₀ monovalent alkyl moiety, or a C₁ to C₁₀ monovalent hydroxyalkyl moiety;

Y¹ is one of: a hydrogen atom; a hydroxyl moiety; a monovalent C₁ to C₅ alkyl moiety; a monovalent C₁ to C₅ hydroxyalkyl moiety; a monovalent C₆ to C₁₂ aryl, benzyl, or benzo moiety; or a moiety conforming to general formula (III):



in which, independently for each unit according to general formula (I) in which Y¹ conforms to general formula (III), each of R³ and R⁴ is independently a hydrogen atom, a monovalent C₁ to C₁₀ alkyl moiety, or a monovalent C₁ to C₁₀ hydroxyalkyl moiety, and X² is a hydrogen atom or a moiety Z² conforming to general formula (IV):



in which each of R⁵ and R⁶ is independently a hydrogen atom, a monovalent C₁ to C₁₀ alkyl moiety, or a monovalent C₁ to C₁₀ hydroxyalkyl moiety;

or Y¹ and Y² are bonded to each other and to adjacent carbon atoms in the aromatic ring shown in general formula (I) so as to constitute from Y¹, Y², and the aromatic ring shown in general formula (I) a naphthyl or alkyl substituted naphthyl moiety; and

Y² is a hydrogen atom unless it is bonded to Y¹ to constitute part of a naphthyl moiety as described above;

said polymer molecules that comprise, preferably consist essentially of, or more preferably, except for end groups, consist of structural units conforming to general formula (I), having a total number of Z¹ and Z² moieties and a distinct (but not necessarily unequal) total number of units conforming to general formula (I) and Y¹ moieties that conform to general formula (III), such that the total number of Z¹ and Z² moieties has a ratio to the total number of units conforming to general formula (I) and Y¹ moieties that conform to general formula (III) that is from 0.2:1.0 to 1.0:1.0. As an example, when the polymer contains 100 structural units with formula (I) and 100 total Z¹ and Z² moieties are present in this polymer, this ratio will be 1.0 when none of the Y¹ moieties corresponds to gen-

eral formula (III) and will be 0.5 when every Y¹ moiety corresponds to general formula (III).

Detailed Description of the Invention

5 Y¹ in general formula (I) is preferably a group conforming to general formula (III), because this provides an increased adherence between the laminated film and the metal.

10 In addition, phosphoric acid-type compounds and/or organosilicon compounds are preferably present in the coating on the subject coated metal, because this also provides an increased adherence between the laminated film and the metal.

The coating under discussion can be executed on the metal as a reactive coating or a dry-in-place coating. "Reactive" denotes treatment in which reaction is effected with the metal surface, the residual unreacted aqueous liquid composition, hereinafter often called "bath" for brevity, even if contacted with the surface by some method such as spraying, on the surface is then removed by a water rinse, and the metal is thereafter dried. "Dry-in-place" denotes treatment in which bath is applied to the metal surface followed by drying without an intervening water rinse.

A process according to the present invention for preparation of the reactively coated metal comprises steps of:

- 5 (I) providing a waterborne composition comprising water and at least 0.1 g/L of the above-described polymer comprising units according to general formula (I) and, optionally, at least one selection from phosphoric acid-type compounds and organosilicon compounds, said waterborne composition having a pH in a range from 2.5 to 6.5, the total concentration of one or more selections from phosphoric acid-type compounds and organosilicon compounds preferably being at least 0.1 g/L;
- 10 (II) forming a coating for film lamination on a surface of a metal by contacting and reacting the surface of the metal with said waterborne composition; and
- (III) after step (II), rinsing the metal surface with water and thereafter drying the metal surface.

15 A process according to the present invention for the preparation of a dry-in-place coated metal comprises steps of:

- (I') preparing a waterborne composition comprising water and at least 0.01 g/L of the above-described polymer comprising units according to general formula (I) and, optionally, one or more selections from phosphoric acid-type compounds and organosilicon compounds, said waterborne composition having a pH in a

range from 2.5 to 6.5, the total concentration of one or more selections from phosphoric acid-type compounds and organosilicon compounds preferably being at least 0.1 g/L; and

(II') forming a coating for film lamination on a surface of a metal by application of said waterborne composition to the surface of the metal, and then drying the metal surface.

The metal substrate to be coated according to the present invention is not critical, but in industrial applications will mainly be iron or steel stock or aluminum stock. The shape of the metal is also not critical and is exemplified by shapes that facilitate and support film lamination, such as plate, disk, sheet, and coil shapes.

X¹ in formula (I) for the polymer used for the coated metal according to the present invention is, as specified above, independently selected for each structural unit from the hydrogen atom and groups Z¹ with formula (II). R¹ and R² in formula (II) are independently a hydrogen atom, a C₁ to C₁₀ alkyl moiety, or a C₁ to C₁₀ hydroxyalkyl moiety. Alkyl and hydroxyalkyl having 11 or more carbons usually cause the functional group to be too bulky and result in a coarsening of the coating and hence a decline in the corrosion resistance. More preferably, at least in part for reasons of economical commercial availability, these alkyl moieties and hydroxyalkyl moieties have not more than, with increasing preference in the order given, 8, 6, 4, 3, or 2 carbon atoms each.

As specified above, Y¹ in general formula (I) may be a hydrogen atom, a hydroxyl moiety, a C₁ to C₅ alkyl moiety, a C₁ to C₅ hydroxyalkyl moiety, a C₆ to C₁₂ aryl, benzyl, or benzo moiety, or a moiety conforming to general formula (III). In addition Y¹ and Y² can together form a naphthyl moiety that includes the carbon atoms of the aromatic ring shown in formula (I). Alkyl and hydroxyalkyl moieties having 6 or more carbons and aryl moieties having 13 or more carbons usually cause the resin to become bulky and develop steric hindrance and thereby prevent the coating from assuming the fine, dense configuration that exhibits excellent corrosion resistance and excellent adherence. More preferably, at least in part for reasons of economical commercial availability, these alkyl and hydroxyalkyl moieties have not more than, with increasing preference in the order given, 8, 6, 4, 3, or 2 carbon atoms each. Y¹ is preferably a group with formula (III) for the good adherence this favors.

If the total number of Z¹ and Z² moieties has a ratio to the total number of units conforming to general formula (I) and Y¹ moieties that conform to general formula (III) that is less than 0.2, the resin normally will not exhibit an acceptable adherence to the metal and the film will readily debond during working operations. Preferably, in order to

more thoroughly avoid any difficulties with the adhesion of the resin to either the film or the metal, this ratio is at least 0.5. A value for this ratio in excess of 1.0:1.0 usually causes an excessive bulkiness and hence a coarse coating and a reduced corrosion resistance.

5 The usual methods can be used to prepare the polymer (I) that makes up at least part of the coating on the coated metal according to the present invention. For example, polymer conforming to general formula (I) can be synthesized by polycondensing formaldehyde with a phenol, naphthol, or bisphenol (e.g., bisphenol-A or -F) and then introducing the X¹ and X² functional groups using formaldehyde and amine. The usual
10 grades of formalin can be used as the formaldehyde.

While the molecular weight of this polymer is not critical, its molecular weight will generally be from 1,000 to 1,000,000, preferably from 1,000 to 100,000, and particularly preferably from 1,000 to 10,000. The molecular weight can be measured by gel permeation chromatography on the peeled-off coating.

15 As discussed above, a phosphoric acid-type compound and/or an organosilicon compound is preferably present in the coating on the coated metal according to the present invention, because this provides an improved adherence between the laminated film and metal.

Phosphoric acid-type compounds usable for this purpose are exemplified by
20 metaphosphoric acid and its salts, orthophosphoric acid and its salts, condensed phosphoric acids, i.e., acids conforming to the general formula H_(p+2)P_pO_(3p+1), where p is a positive integer with a value of at least 2, preferably 2 or 3, the salts of any of these acids, and stable colloidal dispersions of zirconium phosphate and titanium phosphate(s) in water. The salts are exemplified by the ammonium salts and by the alkali metal salts
25 such as the sodium and potassium salts.

The organosilicon compounds are preferably selected from silanes conforming to general formula (V):



in which R denotes an alkyl moiety, which may be the same or different from one of the
30 m YR and the n R moieties to another; X denotes a methoxy or ethoxy moiety; Y denotes a moiety selected from the group consisting of vinyl, amino, mercapto, and glycidoxy, and methacryloxy moieties, which may be the same or different from one of the m YR moieties to another; m is an integer with a value from 1 to 3; and n is an integer with a value of 0 to (3-m). Such silanes are exemplified by vinyltriethoxysilane, γ-aminopropyltriethoxysilane, N-(β-aminoethyl)-γ-aminopropyltriethoxysilane, γ-mercaptopropyltrimeth-
35

oxysilane, γ -glycidoxypolytrimethoxysilane, and γ -methacryloxypolytrimethoxysilane.

The add-on mass per unit area of the phosphoric acid-type compound, measured as its stoichiometric equivalent as phosphorus, relative to the metal must be at least 0.1 mg/m² in order to achieve the benefit specified above for the addition of this ingredient.

5 The add-on preferably does not exceed 200 mg/m². An increase in the adherence of the laminated film is not observed at an add-on below 0.1 mg/m², while add-ons in excess of 200 mg/m² are costly. The add-on mass per unit area coated of the organosilicon compound, measured as its stoichiometric equivalent as silicon, relative to the metal must be at least 0.1 mg/m² in order to achieve the benefits specified above for the addition of this ingredient. The add-on of silicon preferably does not exceed 100 mg/m². Little if any increase in adherence is observed at an add-on below 0.1 mg/m², while add-ons in excess of 100 mg/m² are costly.

The phosphorus add-on and silicon add-on can be determined using commercially available fluorescent x-ray analyzers. Specifically, a plurality of samples bearing known but different phosphorus (or silicon) add-ons are measured and the corresponding intensity-versus-add-on calibration curve is constructed from the measured intensities in counts per second (hereinafter usually abbreviated as "cps"). A sample is then cut from the coated metal according to the present invention and measured under the same conditions as in calibration. The measured intensity is converted to add-on using the calibration curve.

20 The coating on the coated metal according to the present invention must exhibit a thickness of 5 to 500 nm, preferably has a thickness of 15 to 300 nm, and more preferably of 50 to 300 nm. An excellent adherence by the laminated film is not obtained at coating thicknesses below 5 nm, while exceeding 500 nm has a high potential for impairing the color of the metal. The overall coating weight of the coating must include 5 to 500 mg as carbon per m² and is preferably from 50 to 200 mg/m². An excellent adherence is not obtained when the total coating weight is below 5 mg/m², while exceeding 500 mg/m² has a high potential for impairing the color of the metal.

25 The carbon add-on can be measured using commercially available surface carbon analyzers. Specifically, the coated metal according to the present invention is first cut to a suitable size (about 20 to 50 cm²) to provide the sample. Surface carbon analyzers operate by heating the sample in order to oxidize and volatilize the carbon present on the surface and measuring the resulting gas using infrared (hereinafter usually abbreviated as "IR") absorption. While any measurement conditions can be used that result in oxidation and volatilization of the surface carbon, measurement is

ordinarily preferably run at 400 °C to 500 °C for 5 to 10 minutes.

In addition, the coating on the coated metal according to the present invention must cover at least 90 % of the metal surface. The film has a strong tendency to debond during working operations at coverage ratios below 90 %.

5 The coating thickness and coverage ratio can be measured using commercially available x-ray photoelectron spectroscopic analysis (hereinafter usually abbreviated as "XPS") instruments. In an XPS instrument, the sample is excited by X-rays under an ultrahigh vacuum, i.e., a pressure $\leq 10^{-5}$ Pascal) and the emitted photoelectrons are analyzed. The proportions of the atoms present in the surface can be determined from the
10 intensity of the photoelectrons and a sensitivity factor. The methods for carrying out the quantitative calculation of coating thickness and coverage ratio have already been established and are available as commercial software.

Measurement of the coverage ratio will be considered first. Samples exposed to the atmosphere will inevitably be contaminated. Thus, XPS analysis of a sample
15 cleaned in the atmosphere will detect contaminants such as carbon in the outermost surface. In order to eliminate this interference, in the present invention analysis for determination of the coverage ratio was carried out after a moderate sputtering with argon that removed 2 nm of the outermost surface. In sequence, the surface was first sputtered, using a commercial argon sputtering gun attached to the XPS analyzer, in order
20 to remove contaminants, the surface was then excited by X-rays, and the photoelectron emission was analyzed. After X-ray excitation, a so-called wide-scan analysis was run in order to qualitate the atoms present in the surface. In the present invention the elements generally detected in analysis of the coating were mainly carbon, oxygen, phosphorus, silicon, zirconium, titanium, and the elements in the metal stock (iron, aluminum).
25 Quantitative calculation was carried out on the qualitatively measured elements and a value "A", the total atomic % for the atoms constituting the metal substrate, was determined from this. The coverage ratio percentage was defined to be $100 - A$.

The coating thickness was then measured using the argon sputtering gun. The coating thickness was first measured on a plural number of samples having different but
30 known coating thicknesses that had been measured using a transmission electron microscope. Each of these samples was repeatedly subjected to argon sputtering followed by photoelectron analysis. The coating was assumed to be present until the coverage ratio reached 40 %. A calibration curve was constructed from the known coating thicknesses and the total time required in each case for sputtering to the end point.
35 In the subsequent analyses of samples of coated metal according to the present inven-

tion, the coating thickness was determined from the calibration curve using the total sputtering time to reach a coverage ratio of 40 %.

Methods for the preparation of the coated metal according to the present invention will now be considered in detail.

5 The surface of the metal stock normally must be cleaned before fabrication of the coated metal according to the present invention comprising metal bearing a coating for film lamination. Thus, industrial metal stock normally carries rolling oil or is coated with rust-preventive oil, and these oils must be removed, by a process generally known as degreasing. The degreasing technique is not critical, and solvent degreasers, alkaline
10 degreasers, and acidic degreasers in general use as known to those skilled in the art can be used for this purpose.

 The pH of a composition according to this invention is preferably 3.0 to 5.0. A satisfactory coating formation does not usually occur at a pH below 2.5, while problems with the stability of the waterborne composition often occur at a pH above 6.5. The pH
15 can be adjusted as necessary using sodium hydroxide or an acid such as phosphoric acid, condensed phosphoric acid, hydrofluoric acid, etc., and particularly mineral acids. The acids function as etchants. The etching efficiency can be increased through the use of peroxide and the like as an etching assistant.

 The concentration of polymer comprising units that conform to general formula
20 (I) must be at least 0.1 g/L, is preferably from 0.1 to 10 g/L, and more preferably is from 0.3 to 3 g/L. A satisfactory coating formation does not occur when the polymer concentration is less than 0.1 g/L, while high costs, without adequately corresponding benefits, are incurred when the polymer concentration exceeds 10 g/L. The concentration of the one or more selections from phosphoric acid-type compounds and organosilicon com-
25 pounds preferably is at least 0.1 g/L, is more preferably from 0.1 to 30 g/L, and still more preferably is from 0.3 to 1 g/L. The reactivity may be undesirably low when the concentration of the one or more selections from phosphoric acid-type compounds and organosilicon compounds is below 0.1 g/L, while high costs, without adequately corresponding benefits, are incurred when this concentration exceeds 30 g/L.

30 The technique for effecting contact between the waterborne composition and the metal is not critical. Contact is normally effected by spraying the metal surface with the waterborne composition or dipping the metal in the waterborne composition. The temperature of the waterborne composition during this treatment is not critical, but is generally preferably from 40 °C to 60 °C. When spraying is used, the metal is preferably al-
35 lowed to stand for about 1 to 30 seconds after spraying. When dipping is used, the

dipping time is preferably from about 1 to 30 seconds. During this contact the surface of the metal is etched and a local increase in pH occurs at the interface. This results in coating due to deposition of the polymer on the surface. When a reactive coating is being formed, unreacted bath is ordinarily removed by rinsing with water after the contact phase. The coating is usually then dried. While the drying temperature is not critical, drying temperatures of 60 °C to 200 °C are ordinarily preferred. Drying is generally effected using a hot gas flow; air is generally the most economical and readily available gas for this purpose.

The coating thickness, coating weight, coverage ratio, phosphoric acid-type compound add-on, and organosilicon compound add-on for the dried coating are adjusted if necessary into the above-specified ranges in the coated metal according to the present invention. These adjustments can be accomplished by varying such parameters as the concentrations of the polymer, etchant, phosphoric acid-type compound, and organosilicon compound in the waterborne composition, the treatment temperature, the treatment time, and so forth.

The advantages to reactive coating are that it affords very uniform coatings and achieves high coverage ratios at low coating thicknesses.

For dry-in-place coating in a process according to the invention, the concentration of polymer comprising units conforming to general formula (I) is preferably from 0.01 to 10 g/L and more preferably is from 0.1 to 2 g/L. A satisfactory add-on is not obtained when the polymer concentration is less than 0.01 g/L, while high costs, without adequately corresponding benefits, are incurred when the polymer concentration exceeds 10 g/L. The concentration of the one or more selections from phosphoric acid-type compounds and organosilicon compounds preferably is at least 0.01 g/L, is more preferably from 0.01 to 30 g/L, and still more preferably is from 0.05 to 3 g/L. The add-on may be inadequate when the concentration of the one or more selections from phosphoric acid-type compounds and organosilicon compounds is below 0.01 g/L, while high costs, without adequately corresponding benefits, are incurred when this concentration exceeds 30 g/L.

Unlike the case of reactive coating, the waterborne composition can have any pH in the case of dry-in-place coating and the pH is therefore not critical. However, a pH from 3 to 6 will generally be suitable.

The technique for applying the waterborne composition to the metal surface is not critical in the case of dry-in-place coating, but in general the waterborne composition will be applied to the metal surface using, for example, a roll coater. The temperature

of the waterborne composition during application is not critical, but temperatures from 15 °C to 35 °C are generally preferred. The coating is usually then dried. The drying temperature is again not critical, but temperatures from 80 °C to 200 °C are generally preferred. Drying will generally be carried out using a hot gas flow, with air again
5 normally the most economical and readily available gas for this purpose.

The coating thickness, coating weight, coverage ratio, phosphoric acid-type compound add-on, and organosilicon compound add-on for the dried coating are adjusted if needed into the above-specified ranges in the coated metal according to the present invention. These adjustments can be accomplished by adjusting such parameters as
10 the concentrations of the polymer, phosphoric acid-type compound, and organosilicon compound in the waterborne composition and the application temperature.

The advantage to dry-in-place coating is that this treatment can be run as one element in a continuous process. In other words, dry-in-place coating formation can be run as a pre-treatment when film lamination is being run as a continuous process.

15 The same methods used for film lamination on prior-art coated metals bearing a chromium-type coating can be used for film lamination on coated metal according to the present invention bearing on its surface a coating for film lamination generated as described above.

The nature of the laminated film is not critical, and conventional lamination films
20 as referenced in the preceding description of the prior art can be used. The film is specifically exemplified by thermoplastic resin films, e.g., polyethylene films, polycarbonate films, and polyester films and particularly films composed mainly of polymers of vinyl terephthalate. The shape of the lamination film is not critical, but in general plate-shaped films or sheet-form films will be used. While the film lamination technology is not
25 critical, lamination is typically carried out by heating and softening the film. The use of adhesive at this point is not generally necessary, but an adhesive may be used as desired.

Several examples of the coating according to the present invention are provided below. Moreover, the utility of these coatings is described relative to comparative
30 examples.

Substrate Metals and Cleaning Processes Used

1. Aluminum alloy sheet

The surface of commercial aluminum-manganese alloy sheet (Japanese Industrial Standard, hereinafter usually abbreviated as "JIS", type A3004, sheet thickness = 0.3
35 mm, dimensions = 200 × 300 mm) was cleaned by spraying for 20 seconds at 75 °C

with an 8 % aqueous solution of a commercial acidic cleaner (PALKLIN® 500 from Nihon Parkerizing Company, Limited). This was followed by a water rinse.

2. Steel sheet

The surface of commercial cold-rolled steel sheet (JIS type SPCC, sheet thickness = 0.3 mm, dimensions = 200 × 300 mm) was cleaned by spraying for 20 seconds at 60 °C with a 2 % aqueous solution of a commercial cleaner (Fine Cleaner 4328 from Nihon Parkerizing Company, Limited). This was followed by a water rinse.

Production of the Coated Metals

The aluminum alloy or steel sheet was coated as described in the particular example or comparative example to form thereon a reactive coating or a dry-in-place coating.

Measurement of the Carbon Add-on

The carbon add-on (mg/m²) by the coating was measured using a commercial surface carbon analyzer from LECO. The sample size was 32 cm² and the measurement conditions were 400 °C for 8 minutes.

Coverage Ratio and Coating Thickness

The status of the coating was analyzed using a commercial XPS (X-ray photoelectron spectroscopic analysis) instrument from Shimadzu. Mg was used as the X-ray source at conditions of 8 kilovolts and 30 milliamperes (hereinafter usually abbreviated as "mA"). The sample size was a circle 5 mm in diameter. Qualitative analysis was carried out after a 2 nm sputtering of the outermost surface. The detected elements were quantitatively calculated and the coverage ratio was then calculated as described above. A commercial argon sputtering gun (Shimadzu) was attached to the XPS instrument and the coating was destroyed and removed by sputtering. The sputtering conditions were 600 volts and 50 milliamperes. The coating thickness (nm) was determined from the sputtering time using the method described above.

Film Lamination and Forming

The coated metal was laminated with polyester film (thickness = 30 μm) at 180 °C and then punched to form a circular disk 140 mm in diameter, and this was drawn to give a cup. The cup was subsequently re-drawn and ironed using a three-piece die to give the draw-ironed can.

Performance Evaluation of the Film-Laminated Coated Metal

1. Formability

The draw-ironing process was evaluated on the following scale.

x : rupture

Δ : scarring without rupture

+

2. Corrosion resistance

The leakage current was measured on the draw-ironed can body using a commercial enamel rater from the Peco Company. The measurement liquid was 0.5 % saline, and the current value, at 6.3 volts potential difference, was measured after 4 seconds. Lower current values are desirable. The results were scored on the following scale.

+

Δ : at least 0.3 mA, but less than 1.0 mA

x : 1.0 mA or more

3. Adherence

The draw-ironed can body was retorted, i.e., heated in steam under pressure, in a commercial sterilizer at 121 °C for 30 minutes. The adherence was evaluated on the following scale based on the post-retorting adherence of the film.

+

Δ : partial debonding

x : debonding over the entire surface

4. Environmental safety

The use of hexavalent chromium, which is toxic to humans, during formation of the coating was scored with the symbol x, while the non-use of hexavalent chromium was scored with the symbol +.

Example 1

A dry-in-place coating was produced by applying the Waterborne Composition 1 described below to the aluminum alloy sheet specified above and then drying the coating at 80 °C.

Waterborne Composition 1

Water Soluble Polymer 1 solids 2.0 g/L
pH 6.0 (adjusted with phosphoric acid)

Water Soluble Polymer 1

This was a polymer consisting entirely, except for short end groups, of units represented by formula (I) when: X¹ in each structural unit conforming to general formula (I) was a hydrogen atom or a moiety -CH₂N(CH₃)₂, corresponding to Z¹; Y¹ and Y² each represents a hydrogen atom; and the average ratio of Z¹ moieties to benzene rings was 0.5:1.0. The polymer had a weight average molecular weight of

3,000.

Example 2

A dry-in-place coating was produced by applying Waterborne Composition 2 described below to the aluminum alloy sheet specified above and then drying the coating at 80 °C.

Waterborne Composition 2

| | | |
|--|-----|-----|
| Water Soluble Polymer 2 solids | 0.5 | g/L |
| pH 6.0 (adjusted with phosphoric acid) | | |

Water Soluble Polymer 2

This was a polymer consisting entirely, except for short end groups, of units represented by formula (I) when: X¹ in each structural unit conforming to general formula (I) was a hydrogen atom or a moiety -CH₂N(CH₃)₂, corresponding to Z¹; Y¹ conformed to general formula (III) when: X² represents a hydrogen atom or a moiety -CH₂N(CH₃)₂, corresponding to Z²; Y² represents a hydrogen atom; and the average ratio of the total -CH₂N(CH₃)₂ moieties, corresponding to Z¹+Z², to benzene rings was 1.0:1.0. The polymer had a weight average molecular weight of 1,500.

Example 3

A reactive coating was produced by spraying Waterborne Composition 3 for 20 seconds at a composition temperature of 50 °C onto the aluminum alloy sheet specified above, rinsing the surface with water and then deionized water, and then drying the coating at 80 °C.

Waterborne Composition 3

| | | |
|---|------|-----|
| HF | 0.05 | g/L |
| H ₃ PO ₄ | 2.0 | g/L |
| Na ₄ P ₂ O ₇ ·10H ₂ O | 2.0 | g/L |
| Water Soluble Polymer 3 solids | 5.0 | g/L |
| pH 4.0 (adjusted with sodium hydroxide) | | |

Water Soluble Polymer 3

This was a polymer consisting entirely, except for short end groups, of units conforming to formula (I) when X¹ is a hydrogen atom or a moiety -CH₂N(CH₂CH₂OH)₂, corresponding to Z¹; Y¹ conforms to general formula (III) when X² is a hydrogen atom or a moiety -CH₂N(CH₂CH₂OH)₂, corresponding to Z²; Y² represents a hydrogen atom; and the average ratio of Z¹+Z² moieties to benzene rings is 0.75:1.0. The polymer had a weight average molecular weight of 5,000.

Example 4

A reactive coating was produced by dipping the aluminum alloy sheet specified above in Waterborne Composition 4 for 4 seconds at a composition temperature of 60 °C, rinsing the surface with water and then deionized water, and then drying the coating at 80 °C.

Waterborne Composition 4

| | | |
|--|------|-----|
| HF | 0.05 | g/L |
| H ₂ O ₂ | 1.0 | g/L |
| H ₃ PO ₄ | 2.0 | g/L |
| Na ₄ P ₂ O ₇ · 10H ₂ O | 2.0 | g/L |
| Water Soluble Polymer 4 solids | 5.0 | g/L |

pH 3.5 (adjusted with sodium hydroxide)

Water Soluble Polymer 4

This was a polymer consisting entirely, except for short end groups, of units conforming to formula (I) when: X¹ is a hydrogen atom or a moiety

-CH₂N(CH₂CH₂CH₂OH)(CH₃), corresponding to Z¹; Y¹ conforms to general formula (III) when X² is a hydrogen atom or a moiety -CH₂N(CH₂CH₂CH₂OH)(CH₃), corresponding to Z²; Y² represents a hydrogen atom; and the average ratio of Z¹ + Z² moieties per benzene ring is 0.5:1.0. The polymer had a weight average molecular weight of 7,500.

Example 5

A dry-in-place coating was produced by applying the Waterborne Composition 5 described below to the steel sheet specified above and then drying the coating at 80 °C.

Waterborne Composition 5

| | | |
|---------------------------------|-----|-----|
| Water Soluble Polymer 1 solids | 2.0 | g/L |
| H ₂ ZrF ₆ | 0.1 | g/L |
| H ₃ PO ₄ | 0.1 | g/L |

pH 6.0 (adjusted with aqueous ammonia)

Example 6

A dry-in-place coating was produced by applying the Waterborne Composition 6 described below to the steel sheet specified above and then drying the coating at 80 °C.

Waterborne Composition 6

| | | |
|--------------------------------|-----|-----|
| Water Soluble Polymer 3 solids | 2.0 | g/L |
|--------------------------------|-----|-----|

| | | |
|---|------|-----|
| H_2ZrF_6 | 0.1 | g/L |
| H_3PO_4 | 0.1 | g/L |
| γ -glycidoxypropyltrimethoxysilane | 0.05 | g/L |
| pH 6.0 (adjusted with aqueous ammonia) | | |

5 Example 7

A reactive coating was produced by dipping the steel sheet specified above in Waterborne Composition 7 for 10 seconds at a composition temperature of 60 °C, rinsing the surface with water and then deionized water, and then drying the coating at 80 °C.

10 Waterborne Composition 7

| | | |
|--------------------------------------|------|-----|
| HF | 0.10 | g/L |
| H_2O_2 | 2.0 | g/L |
| H_3PO_4 | 2.0 | g/L |
| $Na_4P_2O_7 \cdot 10H_2O$ | 2.0 | g/L |
| 15 Water Soluble Polymer 3 solids | 5.0 | g/L |

pH 4.0 (adjusted with sodium hydroxide)

Comparative Example 1

A coating was produced by spraying the above-specified aluminum alloy sheet for 10 seconds at a solution temperature of 50 °C with a 4 % aqueous solution of a commercial phosphate-chromate conversion agent (ALCHROME® K 702 from Nihon Parkerizing Company, Limited) followed by rinsing the surface with water and then deionized water and then drying the coating at 80 °C.

Comparative Example 2

A coating was produced by spraying the above-specified aluminum alloy sheet for 10 seconds at a solution temperature of 40 °C with a 2 % aqueous solution of a commercial zirconium-type conversion agent (ALODINE® N 405 from Nihon Parkerizing Company, Limited) followed by rinsing the surface with water and then deionized water and then drying the coating at 80 °C.

Comparative Example 3

A coating was produced by applying the Waterborne Composition 8 described below to the steel sheet specified above and then drying the coating at 80 °C.

Waterborne Composition 8

| | | |
|--|------|-----|
| H_2ZrF_6 | 0.1 | g/L |
| H_3PO_4 | 0.1 | g/L |
| 35 γ -glycidoxypropyltrimethoxysilane | 0.05 | g/L |

pH 6.0 (adjusted with aqueous ammonia)

Comparative Example 4

Commercial TFS on which a chromium-type coating had been executed was used.

5 Table 1 below reports the coating thickness, carbon add-on, and coverage ratio for the coated metals prepared in Examples 1 to 7 and Comparative Examples 1 to 4.

Table 1

| Example ("Ex") or Com- parison Example ("CE") Number | Treatment Characteristics | | Characteristics of the Coating Formed During Treatment | | | | |
|--|------------------------------|-------------------|--|--|---------------------------|--|----|
| | Sub- strate | Contact Method | Coating Thick- ness, nm | Carbon Add-On Mass, mg/m ² | Cover- age Ratio, % | Optional Element Add-On Masses, mg/m ² , for: | |
| | | | | | | P | Si |
| Ex 1 | Al | dry-in-place | 200 | 200 | 96 | 5 | 0 |
| Ex 2 | Al | dry-in-place | 100 | 100 | 90 | 5 | 0 |
| Ex 3 | Al | reactive | 20 | 20 | 95 | 3 | 0 |
| Ex 4 | Al | reactive | 30 | 30 | 97 | 3 | 0 |
| Ex 5 | steel | dry-in-place | 250 | 250 | 95 | 10 | 0 |
| Ex 6 | steel | dry-in-place | 250 | 250 | 95 | 5 | 2 |
| Ex 7 | steel | reactive | 15 | 15 | 90 | 2 | 0 |
| CE 1 | Al | reactive | 50 | 2 ¹ | 85 | 10 | 0 |
| CE 2 | Al | reactive | 25 | 2 ¹ | 85 | 5 | 0 |
| CE 3 | steel | dry-in-place | 100 | 2 ¹ | 80 | 4 | 1 |
| CE 4 | TFS | none | - | 2 ¹ | - | 0 | 0 |

Footnotes for Table 1

¹Detection originating with surface contamination from the atmosphere.

5 Table 2 reports the results from the performance evaluations of the coated metals. As the results in Table 1 make clear, the coated metals in Examples 1 to 7 according to the present invention gave excellent results over the entire property spectrum (formability, corrosion resistance, adherence, and environmental safety). In contrast to this, the property spectrum was not satisfied in its entirety by any of the comparative examples, i.e., Comparative Example 1 in which the coated metal carried a phosphate-

chromate coating, Comparative Example 2 in which the coated metal carried a zirconium-type coating, Comparative Example 3 in which the coated metal carried a coating that did not contain the polymer used by the present invention, and Comparative Example 4, in which the substrate was precoated TFS.

Table 2

| Example ("Ex") or Comparison Example ("CE") Number | Performance Rating for: | | | |
|--|-------------------------|----------------------|-----------|----------------------|
| | Formability | Corrosion Resistance | Adherence | Environmental Safety |
| Ex 1 | + | + | + | + |
| Ex 2 | + | + | + | + |
| Ex 3 | + | + | + | + |
| Ex 4 | + | + | + | + |
| Ex 5 | + | + | + | + |
| Ex 6 | + | + | + | + |
| Ex 7 | + | + | + | + |
| CE 1 | Δ | x | x | x |
| CE 2 | x | *2 | *2 | + |
| CE 3 | x | *2 | *2 | + |
| CE 4 | + | + | + | x |

Footnotes for Table 2

*2No can could be formed. Because the corrosion resistance and adherence tests were performed only on finished cans, the values for these columns in these comparative experiments therefore could not be obtained.

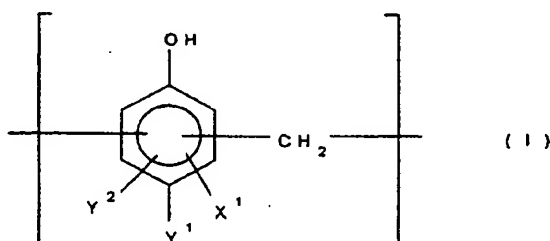
Benefits of the Invention

The coated metal according to the present invention has an excellent formability, excellent corrosion resistance, excellent adherence, and excellent environmental safety.

Claims

1. A coated metal article having on its surface a coating suitable for film lamination thereon, wherein:

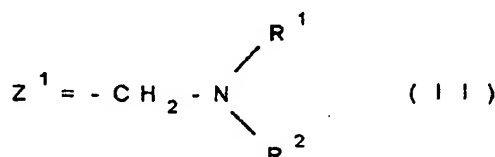
- said coating has a thickness that is from 5 to 500 nm;
- 5 - said coating has a content of carbon atoms that corresponds to from 5 to 500 mg/m² of the coating area;
- said coating covers at least 90 % of the surface of the metal; and
- said coating comprises polymer molecules that comprise units conforming to general formula (I):



15

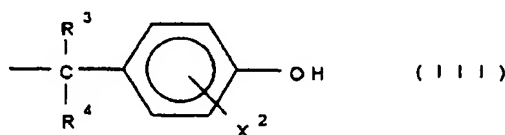
in which:

X¹ independently in each structural unit is a hydrogen atom or a moiety Z¹ conforming to general formula (II):



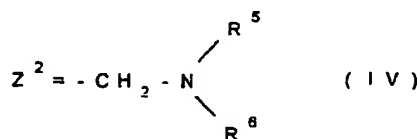
20

in which each of R¹ and R² independently is a hydrogen atom, a C₁ to C₁₀ monovalent alkyl moiety, or a C₁ to C₁₀ monovalent hydroxyalkyl moiety; Y¹, independently for each unit, is a hydrogen atom, a hydroxyl group, a C₁ to C₅ alkyl moiety, a C₁ to C₅ hydroxyalkyl moiety, a C₆ to C₁₂ aryl, benzyl, or benzo moiety, or a moiety conforming to general formula (III):



in which, independently for each unit according to general formula (I) in

which Y¹ conforms to general formula (III), each of R³ and R⁴ is independently a hydrogen atom, a C₁ to C₁₀ alkyl moiety, or a C₁ to C₁₀ hydroxyalkyl moiety, and X² is a hydrogen atom or a moiety Z² conforming to general formula (IV):



in which each of R⁵ and R⁶ is independently a hydrogen atom, a C₁ to C₁₀ alkyl moiety, or a C₁ to C₁₀ hydroxyalkyl moiety;

and

Y², independently for each unit, is a hydrogen atom or, when Y¹ and Y² are bonded to adjacent carbon atoms in the aromatic ring shown in general formula (I), Y¹, Y², and said adjacent carbon atoms to which Y¹ and Y² are bonded together may constitute a condensed benzene ring,

said polymer molecules that comprise structural units conforming to general formula (I) having a total number of Z¹ and Z² moieties and a distinct (but not necessarily unequal) total number of (i) units conforming to general formula (I) and (ii) Y¹ moieties that conform to general formula (III), such that the total number of Z¹ and Z² moieties has a ratio to the total number of units conforming to general formula (I) and Y¹ moieties that conform to general formula (III) that is from 0.2:1.0 to 1.0:1.0.

2. A coated metal article according to claim 1, in which Y¹ in general formula (I) conforms to general formula (III).

3. A coated metal article according to claim 2, in which the coating comprises a total of at least 0.1 mg/m² of phosphorus atoms present in phosphoric acid like compounds and silicon atoms present in organosilicon compounds.

4. A coated metal article according to claim 1, in which the coating comprises a total of at least 0.1 mg/m² of phosphorus atoms present in phosphoric acid like compounds and silicon atoms present in organosilicon compounds.

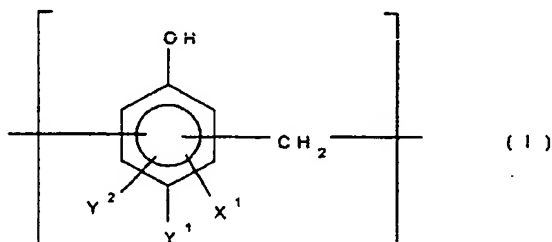
5. A coated metal article according to any one of claims 1 through 4, wherein:

- said coating has a thickness in a range from 50 to 300 nm; and
- said coating has a content of carbon atoms that corresponds to from 50 to 200 mg/m² of the coating area.

6. A process for providing a surface of a metal substrate with a coating suitable for laminating film thereto, said process comprising steps of:

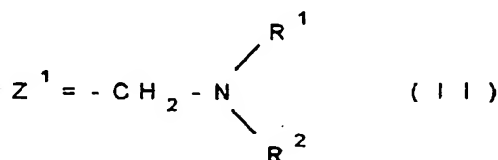
(i) providing a waterborne composition that comprises water and:

10 (A) at least 0.01 g/L of polymer molecules comprising units conforming to general formula (I):



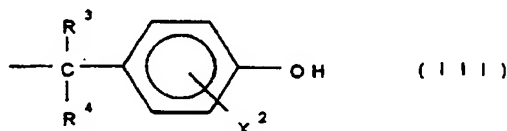
in which:

X^1 , independently in each structural unit, is a hydrogen atom or a moiety Z^1 conforming to general formula (II):



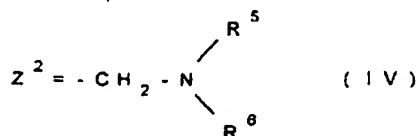
in which each of R^1 and R^2 independently is a hydrogen atom, a C_1 to C_{10} monovalent alkyl moiety, or a C_1 to C_{10} monovalent hydroxyalkyl moiety;

20 Y^1 , independently in each structural unit, is a hydrogen atom, a hydroxyl group, a C_1 to C_5 alkyl moiety, a C_1 to C_5 hydroxyalkyl moiety, a C_6 to C_{12} aryl, benzyl, or benzo moiety, or a moiety conforming to general formula (III):



in which, independently for each unit according to general formula (I) in which Y^1 conforms to general formula (III), each of R^3

and R^4 is independently a hydrogen atom, a C_1 to C_{10} alkyl moiety, or a C_1 to C_{10} hydroxyalkyl moiety, and X^2 is a hydrogen atom or a moiety Z^2 conforming to general formula (IV):



in which each of R^5 and R^6 is independently a hydrogen atom, a C_1 to C_{10} alkyl moiety, or a C_1 to C_{10} hydroxyalkyl moiety;

and

Y^2 , independently in each structural unit, is a hydrogen atom or, when Y^1 and Y^2 are bonded to adjacent carbon atoms in the aromatic ring shown in general formula (I), Y^1 , Y^2 , and said adjacent carbon atoms to which Y^1 and Y^2 are bonded together may constitute a condensed benzene ring,

said polymer molecules that comprise structural units conforming to general formula (I) having a total number of Z^1 and Z^2 moieties and a distinct (but not necessarily unequal) total number of (i) units conforming to general formula (I) and (ii) Y^1 moieties that conform to general formula (III), such that the total number of Z^1 and Z^2 moieties has a ratio to the total number of units conforming to general formula (I) and Y^1 moieties that conform to general formula (III) that is from 0.2:1.0 to 1.0:1.0;

and, optionally, at least one of the following components:

(B) phosphoric acid-type compounds; and

(C) organosilicon compounds,

said waterborne composition having a pH in a range from 2.5 to 6.5;

(II) contacting said surface of said metal substrate with the waterborne composition provided in step (I) for a sufficient time at a sufficient temperature to form a solid coating containing constituents of said waterborne composition, said solid coating adhering to said surface of said metal substrate and being itself covered, at least initially; by a coating of liquid; and

(III) after step (II), drying the metal surface so as to remove from the metal surface the liquid constituents of the coating initially formed in step (II) or of a successor

liquid coating formed by rinsing the surface of said metal substrate as modified after step (II) with water.

7. A process according to claim 6, in which Y^1 in general formula (I) conforms to general formula (III).

8. A process according to claim 7, in which the waterborne composition provided in step (I) comprises a total of at least 0.01 g/l of phosphorus atoms present in phosphoric acid like compounds and silicon atoms present in organosilicon compounds.

9. A process according to claim 6, in which the waterborne composition provided in step (I) comprises a total of at least 0.01 g/l of phosphorus atoms present in phosphoric acid like compounds and silicon atoms present in organosilicon compounds.

10. A process according to claim 7, wherein the waterborne composition provided in step (I) contains at least 0.1 g/L of polymer molecules comprising units conforming to general formula (I) and the coating of liquid formed in step (II) is rinsed with water so as to form a successor coating before completion of step (III).

11. A process according to claim 10, in which the waterborne composition provided in step (I) comprises a total of at least 0.1 g/l of phosphorus atoms present in phosphoric acid like compounds and silicon atoms present in organosilicon compounds.

12. A process according to claim 6, wherein the waterborne composition provided in step (I) contains at least 0.1 g/L of polymer molecules comprising units conforming to general formula (I) and the coating of liquid formed in step (II) is rinsed with water so as to form a successor coating before completion of step (III).

13. A process according to claim 12, in which the waterborne composition provided in step (I) comprises a total of at least 0.1 g/l of phosphorus atoms present in phosphoric acid like compounds and silicon atoms present in organosilicon compounds.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/13685

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C 23C 22/07; B32B 15/08

US CL : 148/253, 257; 427/353; 428/336, 460, 272,3

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/253, 257; 427/353; 428/336, 460, 272,3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Encyclopedia of Polymer Science and Engineering

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: (Phosphate or Phosphoric), (amine?) (p) formaldehyde (p) phenol?, (metal (p) (substrate or layer), Henkel/asn, Yoshida/in, phenolic formaldehyde resin.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-------------|--|--|
| X — Y | US 3,961,992 A (JAHNKE et al.), 8 June 1976, see the entire document especially column 2, lines 38-56; column 3, lines 34-52. | 1, 2, 5, 6, 7, 10, 12 — 8, 9, 11, 13 |
| X — Y | <i>February</i> US 3,868,276 A (SHATZ et al.) 25 February 1975, see the formula on column 3, examples 1-29, and column 1, lines 17-27 | 1-5 — 8, 9, 11, 13 |
| X | US 2,494,297 A (HEMPEL), 10 January 1950, see column 1, lines 20-21; column 2, lines 5-11. | 1, 2, 5 |
| A | US 2,392,574 A (BROWN), 8 January 1946, see column 5, lines 7+; claims 6 and 9 | 1-17 |
| A | US 2,448,397 A (SCHILLING et al.) 31 August 1948, see column 1, lines 9-22 | 3, 4, 8, 9, 11, and 13 |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | |
|--|---|
| * Special categories of cited documents: | *T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| *A document defining the general state of the art which is not considered to be of particular relevance | *X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| *E earlier document published on or after the international filing date | *Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *A document member of the same patent family |
| *O document referring to an oral disclosure, use, exhibition or other means | |
| *P document published prior to the international filing date but later than the priority date claimed | |

Date of the actual completion of the international search

22 OCTOBER 1997

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Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

D. LAWRENCE TARZANOS

Telephone No. (703) 308-2379

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/13685

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|--|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US 2,585,197 A (WALTON) 12 February 1952, see the entire document regarding phenolic - formaldehyde resins with amine functional groups. | 1-13 |
| A | US 4,963,596 A (LINDERT et al.), 16 October 1990, see column 4, lines 10+. | 1-17 |
| A | US 5,125,989 A (HALLMAN) 30 June 1992, see column 3, lines 20+. | 1-17 |
| A | US 5,298,289 A (LINDERT et al.) 29 March 1994, see column 3, lines 40+. | 1-17 |

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平10-46101

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| (51)Int.Cl. ⁶ | 識別記号 | 庁内整理番号 | F I | 技術表示箇所 |
| C 0 9 D 161/08 | P H E | | C 0 9 D 161/08 | P H E |
| C 2 3 C 22/07 | | | C 2 3 C 22/07 | |

審査請求 未請求 請求項の数 7 F D (全 11 頁)

| | |
|----------|----------------|
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| (22)出願日 | 平成8年(1996)8月1日 |

| | |
|---------|--|
| (71)出願人 | 000229597 日本パーカライジング株式会社 東京都中央区日本橋1丁目15番1号 |
| (72)発明者 | 吉田 昌之 東京都中央区日本橋一丁目15番1号 日本 パーカライジング株式会社内 |
| (72)発明者 | 江原 良治 東京都中央区日本橋一丁目15番1号 日本 パーカライジング株式会社内 |
| (74)代理人 | 弁理士 坂口 昇造 |

(54)【発明の名称】 金属材料の表面にフィルムラミネート用下地皮膜を形成させた被覆金属材料、およびその製造方法

(57)【要約】

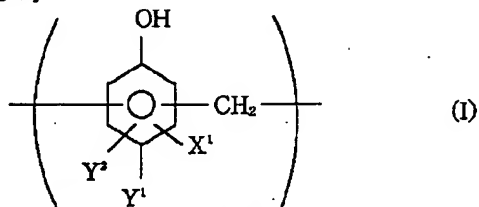
【課題】 金属材料の表面にフィルムラミネート用下地皮膜を形成させた被覆金属材料において、成形性、耐食性、ラミネートフィルム密着性および環境安全性に優れた被覆金属材料、およびその製造方法の提供。

【解決手段】 金属材料の表面にフィルムラミネート用下地皮膜を形成させた被覆金属材料であって、皮膜が特定構造単位よりなるフェノール、ナフトールもしくはビスフェノール-ホルムアルデヒド樹脂からなり、皮膜厚が5~500nmであり、皮膜の全付着量が炭素として5~500mg/m²であり、かつ該皮膜が金属材料表面の90%以上を被覆している該被覆金属材料、およびその製造方法。

【特許請求の範囲】

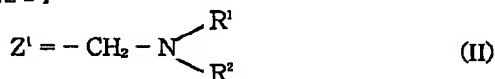
【請求項1】 金属材料の表面にフィルムラミネート用下地皮膜を形成させた被覆金属材料であって、皮膜が下記式(I)で示される構成単位よりなる重合体からなり、皮膜厚が5～500nmであり、皮膜の全付着量が炭素として5～500mg/m²であり、かつ該皮膜が金属材料表面の90%以上を被覆している該被覆金属材料:

【化1】



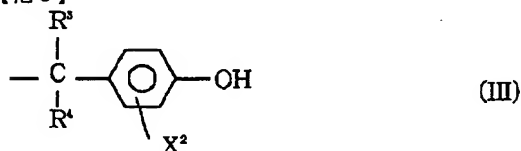
【式中、X¹はそれぞれの構成単位において独立に水素原子または下記式(II)】

【化2】



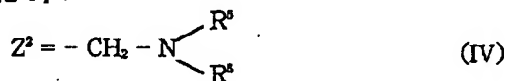
(式中、R¹およびR²は、互いに独立に、水素原子、C₁～C₁₀のアルキル基またはC₁～C₁₀のヒドロキシルアルキル基を表す)で表されるZ¹基を表し、Y¹およびY²は、Y¹が水素原子、水酸基、C₁～C₅のアルキル基、C₁～C₅のヒドロキシルアルキル基、C₆～C₁₂のアリール基、ベンジル基または下記式(III)】

【化3】



(式中、R³およびR⁴は、互いに独立に、水素原子、C₁～C₁₀のアルキル基、またはC₁～C₁₀のヒドロキシルアルキル基を表し、X²は、Y¹が上記式(II)で表される基である場合、式(I)で表されるそれぞれの構成単位において独立に水素原子または下記式(IV)】

【化4】



(式中、R⁵およびR⁶は、互いに独立に、水素原子、C₁～C₁₀のアルキル基、またはC₁～C₁₀のヒドロキシルアルキル基を表す)で表されるZ²基を表す)で表される基を表し、Y²が水素原子を表すか、またはY¹とY¹に隣接する位置に存在する場合のY²がY¹とY²との間の結合も含めて一体となって縮合ベンゼン環を表し、ここにおいて、Z¹基+Z²基の導入率はベンゼン環1個あたり0.2～1.0個である]。

【請求項2】 式(I)においてYが式(III)で表される基である請求項1記載の被覆金属材料。

【請求項3】 皮膜中にリン酸系化合物を金属材料に対しリンとして0.1mg/m²以上含有している請求項1記載の被覆金属材料。

【請求項4】 皮膜中に有機ケイ素化合物を金属材料に対しケイ素として0.1mg/m²以上含有している請求項1記載の被覆金属材料。

【請求項5】 請求項1記載の重合体と水からなり、pHを2.5～6.5に調整した水系組成物であって、重合体の濃度が0.1g/L以上である該水系組成物を金属材料の表面と接触させて該表面と反応させることによりフィルムラミネート用下地皮膜を形成させ、ついで該表面を水洗、乾燥することを特徴とする被覆金属材料の製造方法。

【請求項6】 請求項1記載の重合体と水からなる水系組成物であって、重合体の濃度が0.01g/L以上である該水系組成物を金属材料の表面に塗布して該表面にフィルムラミネート用下地皮膜を形成させ、ついで該表面を乾燥することを特徴とする被覆金属材料の製造方法。

【請求項7】 水系組成物がリン酸系化合物および有機ケイ素化合物の少なくとも1種を0.01g/L以上含有する請求項5項または6項記載の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、フィルムをラミネートする金属材料の表面に、このフィルムと金属材料表面との密着性を高め、かつラミネートされた金属材料の耐食性を向上させる、フィルムラミネート用の下地皮膜を形成させた被覆金属材料、およびその製造方法に関する。さらに詳しくは、フィルムがラミネートされた金属材料を絞り加工や絞りしごき加工、ストレッチドロー加工等の厳しい加工に付しても、フィルムが剥離しないような高いフィルム密着性を与え、かつフィルムがラミネートされた金属材料およびそれからの成形品に高い耐食性を与える、フィルムラミネート用下地皮膜を形成させた被覆金属材料、およびその製造方法に関する。

【0002】

【従来の技術】金属材料(鉄鋼材料、アルミニウム材料等)の多くは種々の加工がなされた後に塗装され、家電製品やビール等の飲料缶等に広く利用されている。一般に、塗装には、溶剤系もしくは水系の塗料が使用され、その後、焼付けが行われる。この塗装工程において、塗料に起因する廃棄物(廃溶剤等)が産業廃棄物として排出され、また、焼付け時に飛散する有機化合物(溶剤や低分子の化合物)や排ガス(主に炭酸ガス)が大気に放出されている。近年、地球環境保全を目的とし、これら産業廃棄物や排ガスを低減しようとする取組みが行われている。この中で、塗装に代わるものとしてフィルムを

ラミネートする技術が注目されている。

【0003】今までに、フィルムをラミネートし製缶する缶の製造方法やこれに関連する発明が多数提案されている。例えば、軟鋼板にポリエチレンフィルムを被覆し絞りしごき加工する「絞りしごき罐の製造方法（日本特許第1571783号）」、所定の配合度をもつ熱可塑性ポリエステル被覆を接着させた材料を用い製缶した

「絞りしごき罐（日本特許第1711723号）」、結晶性の熱可塑性樹脂を被覆し特定の加工をする「薄肉化深絞り缶の製造方法（特開平2-263523号公報）」、熱可塑性樹脂をエチレンテレフタレート为主体とするポリエステルのフィルムとしこれを被覆した金属板を用いる「被覆深絞り缶の製造方法（特公平7-57385号公報）」、金属板と特定の熱可塑性樹脂の被覆層とからなる積層金属板を使用し高度の薄肉化を行った「薄肉化絞り缶の製造方法（特開平3-133523号公報）」、内側最表面に熱可塑性ポリエステル樹脂の被覆層と無機酸化層、外側表面に展延性金属のメッキ層を備え、メッキ層は特定量のすず層、ニッケル層およびアルミニウム層の1種または2種以上とし、特定の総しごき率となるように薄肉化することによる「絞りしごき罐（日本特許第1670957号）」が挙げられる。

【0004】さらに、加工用ラミネート金属材料の有機被覆材料を配向性熱可塑性樹脂フィルムとし再絞り加工時に結晶化度および配向度が高まるようにすると共に、潤滑剤を含めた特定の絞り条件のもとで加工することにより、深絞り缶に経済的な薄肉化を達成し、かつ被覆材料を強度、耐久性に優れた保護層を形成する「被覆薄肉缶の製造方法（特開平4-91825号公報）」、鋼板面に錫含有金属を被覆率20~80%の範囲で被覆し、さらに金属クロムおよびクロム水和酸化物を被覆し、この缶素材を深絞り缶とする「深絞り缶及びその製造方法（特開平6-218465号公報）」、金属板の両面または片面に、特定の固有粘度を有するポリエステル樹脂層を形成することによって、薄肉化深絞り缶用金属板に要求される優れた加工性、加工耐食性、特に成形された缶胴部における耐デンティング性（耐衝撃加工性）を付与する「耐デンティング性に優れた薄肉化深絞り缶用樹脂被覆金属板（特開平4-224936号公報）」が挙げられる。

【0005】さらに、特定の諸条件を満足する冷延鋼板を基体とする表面処理鋼板の有機樹脂被膜構造物を薄肉化絞り成形することによる「薄肉化絞り缶の製造方法（特公平7-108706号公報）」、鋼板上に特定条件にて錫含有金属を被覆し、さらにその全面に金属クロム、クロム水和酸化物と有機樹脂を順次被覆することにより、耐食性に優れた深絞り缶を製造する「深絞り缶及びその製造方法（特開平5-255864号公報）」、上層がポリカーボネート樹脂、下層がポリエステル樹脂からなる複合樹脂層で金属板を被覆することにより薄肉

化深絞り缶等に適するようにした「ポリカーボネート樹脂被覆金属板およびその製造方法（特開平6-226915号公報）」、金属板の表面をポリカーボネート樹脂とポリエステル樹脂を特定割合でブレンドした樹脂層で被覆することにより、耐低温衝撃加工性に優れるようにした「樹脂被覆金属板およびその製造方法（特開平6-255022号公報）」、レトルト処理を施す前の状態で、金属板近傍のポリエステル樹脂層の結晶化分率と残存二軸配向度を特定することにより、缶用材料に要求される加工性、耐食性に優れ、レトルト処理を施しても缶外面が乳白色化しないようにした「耐熱水性に優れたポリエステル樹脂被覆金属板（特開平6-155660号公報）」が挙げられる。

【0006】さらに、熱可塑性樹脂フィルムを被覆した鋼板において、鋼板表裏面各々にクロム、錫の各メッキ層およびクロム水和酸化物層を特定に形成することにより、加工後のフィルム密着性と耐食性の向上を図った「ラミネート鋼板およびその原板（特開平7-138786号公報）」、缶の内面側のポリエステルフィルムは表面が二軸方向に分子配向され、原子間力顕微鏡で視野の表面から粗い部分を選び出し、測定した突起部の大きいものの3点平均高さを特定して、炭酸飲料を開封したときの泡吹き現象を有効に防止した「缶用被覆金属板及びそれから形成されたシームレス缶（特開平6-238818号公報）」、有機樹脂の主成分の配向結晶を含むポリエステル樹脂の固有粘度と軸配向度と面配向度とを特定することにより、耐衝撃性、耐食性の向上を可能にした「耐衝撃性に優れた2ピース缶（特開平7-178485号公報）」等が挙げられる。

【0007】これらの発明では、密着下地としてクロム酸処理、クロム酸/リン酸処理または電解クロム酸処理で形成された無機酸化物層を使うもの（前記、日本特許1670957号）、金属クロムおよびクロム水和酸化物を使うもの（前記、特開平6-218465号公報）、電解クロム酸処理鋼板、TFS（Tin Free Steel）、クロム水和酸化物皮膜、複層めっき、合金めっきを使うもの（前記、特開平6-224936号公報）、クロムとして3~30mg/m²のクロム水和酸化物皮膜を使うもの（前記、特開平6-226915号公報）、すずメッキ鋼板、TFS（前記、特開平6-138786号公報）等が開示されている。これら発明を大別するとスズメッキとクロム系の皮膜に分けられる。しかしながら、スズは高価であること、クロム系は処理に有害な6価クロムを使用すると入った問題を有している。

【0008】実際に上記開示の発明を利用し製缶工程での塗装工程を省略したシステムが実用化されている。これは、TFSにポリエステル系フィルムをラミネートし、ストレッチドローにて製缶する方法である。この方法では、従来、行われていた塗装工程（塗布・焼付け）

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が省略され、塗膜の代わりをラミネートしたフィルムが果たしている。この技術は飲料缶の新しい製造システムとして非常に注目されている。しかしながら、現状では、フィルムラミネート後に厳しい加工が施されるために缶材料に対してフィルムが高い密着性を有し、加工後も種々の内容物により腐食されない耐食性も兼ね備えていなければならないといった性能を満足するラミネートフィルムまたはラミネート方法は開発されておらず、クロム系の皮膜処理が施されたTFSが独占的に使用されている。しかしながら、先に述べたように、皮膜処理に有害な6価クロムを使用することより、ノンクロム系の処理および処理皮膜が強く望まれているのである。

【0009】

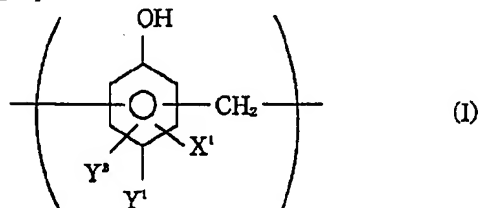
【発明が解決しようとする課題】本発明は前記従来技術の有するこれらの問題点を解決するためのものであり、より具体的には、ノンクロム系のフィルムラミネート用下地皮膜を形成させた被覆金属材料であって、その上にラミネートフィルムを施した場合に、絞り加工や絞りしごき加工、ストレッチドロー加工など厳しい加工工程を経た後においても、優れたラミネートフィルム密着性を示すと共に優れた耐食性を示す該被覆金属材料およびその製造方法を提供することを目的とする。

【0010】

【課題を解決するための手段】本発明者らは、上記目的を達成するための手段について鋭意検討した。その結果、金属材料の表面に、特定の重合体を特定の皮膜厚、特定の付着量および特定の被覆率で被覆した被覆金属材料が該目的を達成することを見出し、本発明を完成した。すなわち、本発明は、金属材料の表面にフィルムラミネート用下地皮膜を形成させた被覆金属材料であって、皮膜が下記式(I)で示される構造単位よりなる重合体からなり、皮膜厚が5~500nmであり、皮膜の全付着量が炭素として5~500mg/m²であり、かつ該皮膜が金属材料表面の90%以上を被覆している該被覆金属材料：

【0011】

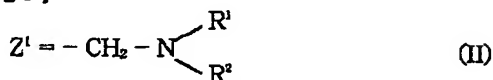
【化5】



【0012】【式中、X¹はそれぞれの構成単位において独立に水素原子または下記式(II)

【0013】

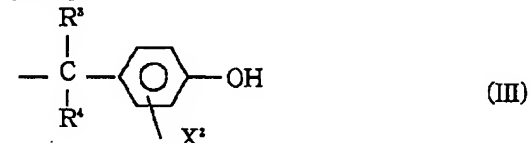
【化6】



【0014】(式中、R¹およびR²は、互いに独立に、水素原子、C₁~C₁₀のアルキル基またはC₁~C₁₀のヒドロキシアルキル基を表す)で表されるZ¹基を表し、Y¹およびY²は、Y¹が水素原子、水酸基、C₁~C₅のアルキル基、C₁~C₅のヒドロキシアルキル基、C₆~C₁₂のアリール基、ベンジル基または下記式(III)

【0015】

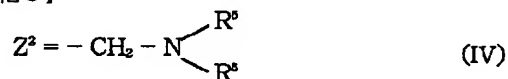
【化7】



【0016】(式中、R³およびR⁴は、互いに独立に、水素原子、C₁~C₁₀のアルキル基、またはC₁~C₁₀のヒドロキシアルキル基を表し、X²は、Y¹が上記式(III)で表される基である場合、式(I)で表されるそれぞれの構成単位において独立に水素原子または下記式(IV)

【0017】

【化8】



【0018】(式中、R⁵およびR⁶は、互いに独立に、水素原子、C₁~C₁₀のアルキル基、またはC₁~C₁₀のヒドロキシアルキル基を表す)で表されるZ²基を表す)で表される基を表し、Y²が水素原子を表すか、またはY¹とY¹に隣接する位置に存在する場合のY²がY¹とY²との間の結合も含めて一体となって縮合ベンゼン環を表し、ここにおいて、Z¹基+Z²基の導入率はベンゼン環1個あたり0.2~1.0個である]に関する。

【0019】上記において、式(I)におけるY¹は式(III)で表される基であることがラミネートフィルムと金属材料との密着性を高める観点から好ましい。また、上記被覆金属材料は皮膜中にリン酸系化合物および/または有機ケイ素化合物を含有していることが、ラミネートフィルムと金属材料との密着性を高める観点から好ましい。上記被覆金属材料は、上記フィルムラミネート用下地皮膜を反応型皮膜として施しても良く、塗布型皮膜として施しても良い。ここで「反応型」とは金属材料表面と反応させて、その後に、表面に残存する未反応物を水洗で除去し、乾燥する処理方法を意味し、塗布型とは、塗布して水洗なしで乾燥する処理方法を意味する。

【0020】反応型皮膜を形成させる場合の被覆金属材料の製造方法として、本発明はまた上記重合体と水からなり、必要に応じリン酸系化合物および有機ケイ素化合物の少なくとも1種を含有し、pHを2.5~6.5に調整した水系組成物であって、重合体の濃度が0.1g

／L以上であり、存在させる場合のリン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度が0.1g／L以上である該水系組成物を金属材料の表面と接触させて該表面と反応させることによりフィルムラミネート用下地皮膜を形成させ、ついで該表面を、水洗、乾燥することを特徴とする被覆金属材料の製造方法に関する。

【0021】塗布型皮膜を形成させる場合の被覆金属材料の製造方法として、本発明はまた上記重合体と水からなり、必要に応じリン酸系化合物および有機ケイ素化合物の少なくとも1種を含有する水系組成物であって、重合体の濃度が0.01g／L以上であり、存在させる場合のリン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度が0.01g／L以上である該水系組成物を金属材料の表面に塗布して該表面にフィルムラミネート用下地皮膜を形成させ、ついで該表面を乾燥することを特徴とする被覆金属材料の製造方法に関する。

【0022】

【発明の実施の形態】以下に本発明の内容について詳しく説明する。本発明の被覆金属材料に用いる金属材料は特に制限されないが、工業上、鉄鋼材料やアルミニウム系材料が主として挙げられる。また、金属材料の形状についても特に制限はないが、フィルムをラミネートしやすい形状、例えば、板状、シート状、コイル状が好ましい。

【0023】本発明の被覆金属材料に用いる重合体については、式(I)中、 X^1 は前記したごとく、それぞれの構成単位において独立に、水素原子または式(II)で表される Z^1 基である。式(II)中、 R^1 、 R^2 は、互いに独立に、水素原子、 $C_1 \sim C_{10}$ のアルキル基または $C_1 \sim C_{10}$ のヒドロキシアルキル基を表すが、 C_{11} 以上のアルキル基またはヒドロキシアルキル基では官能基がバルキーすぎて皮膜が粗となり耐食性が低下する。式(I)中、 Y^1 は前記したごとく、水素原子、水酸基、 $C_1 \sim C_5$ のアルキル基、 $C_1 \sim C_5$ のヒドロキシアルキル基、 $C_6 \sim C_{12}$ のアリール基、ベンジル基、ベンゾ基または式(III)で表される基を表すか、または Y^2 および Y^1 と Y^2 との間の結合と一体となって縮合ベンゼン環を表すが、 C_6 以上のアルキル基もしくはヒドロキシアルキル基または C_{13} 以上のアリール基では樹脂がバルキーとなり立体障害を引き起こし緻密な耐食性、密着性に優れた皮膜にならない。 Y^1 としては密着性の観点から式(III)で表される基が好ましい。

【0024】また、前記したごとく、 Z^1 基+ Z^2 基の導入率はベンゼン環1個あたり0.2～1.0個である。このことは、例えば、前記式(I)で表される構造単位が100個結合してできた重合体であって、 Z^1 基+ Z^2 基が100個導入されているとすると、 Z^1 基+ Z^2 基の導入率は、 Y^1 が式(III)で表される基でない場合には1.0であり、 Y^1 が式(III)で表される基である場合には0.5であることを意味する。 Z^1 基+ Z^2

基の導入率が0.2未満では樹脂と金属材料との密着性が十分でなく、加工時にフィルムが剥離しやすくなる問題がある。 Z^1 基+ Z^2 基の導入率が1より大きいとバルキーすぎて皮膜が粗となり耐食性が低下する可能性がある。

【0025】本発明の被覆金属材料の皮膜を構成する式(I)で表される重合体は常法により製造し得る。例えば、式(I)で表される重合体は、フェノール化合物、ナフトール化合物またはビスフェノール類(ビスフェノールA、F等)とホルムアルデヒドとを重縮合し、ついでホルムアルデヒドとアミンを用いて官能基 X^1 、 X^2 を導入することにより製造し得る。ホルムアルデヒドとしては通常ホルマリンを用いる。重合体の分子量については特に制限はないが、通常1000～100万程度、好ましくは1000～10万程度、特に1000～1万程度であるのが適当である。分子量の測定は皮膜を剥離した後、ゲルパーミエーションクロマトグラフィーによって行うことができる。

【0026】また、前記したごとく、本発明の被覆金属材料は皮膜中にリン酸系化合物および／または有機ケイ素化合物を含有していることが、ラミネートフィルムと金属材料との密着性を高める観点から好ましい。かかる目的に使用し得るリン酸系化合物としては、リン酸もしくはその塩、縮合リン酸もしくはその塩、リン酸ジルコニウム、リン酸チタン等を挙げることができる。ここで塩としてはアンモニウム塩、ナトリウム塩、カリウム塩等のアルカリ金属塩を挙げることができる。また、有機ケイ素化合物としては、ビニルエトキシシラン、 γ -アミノプロピルトリエトキシシラン、N-(β -アミノエチル)- γ -アミノプロピルトリエトキシシラン、 γ -メルカプトプロピルトリメトキシシラン、 γ -グリシドキシプロピルトリメトキシシラン、 γ -メタクリロキシプロピルトリメトキシシラン等が挙げられる。

【0027】リン酸系化合物の金属材料に対する使用量は、上記目的を達成するためには、リンとして0.1mg／ m^2 以上であることが必要であり、200mg／ m^2 以下であることが好ましい。0.1mg／ m^2 未満ではラミネートフィルムの密着性を高める効果が認められず、200mg／ m^2 を超えると、コストが高くなる。

有機ケイ素化合物の金属材料に対する使用量は、上記目的を達成するためには、ケイ素として0.1mg／ m^2 であることが必要であり、100mg／ m^2 以下であることが好ましい。0.1mg／ m^2 未満では密着性を高める効果が乏しく、100mg／ m^2 を超えると、コストが高くなる。なお、リン付着量およびケイ素付着量は市販の蛍光X線分析装置で定量することができる。すなわち、リンまたはケイ素の付着量が既知で付着量の異なるサンプルを複数測定し、この際の強度(cps)より、強度-付着量の検量線を作成する。同様の条件で本発明の被覆金属材料からサンプルを切り出し、測定す

る。この測定強度を検量線に基づき付着量に変換する。

【0028】本発明の被覆金属材料の下地皮膜については皮膜厚が5~500nmであることが必要であり、15~300nmであることが好ましく、50~300nmであることがさらに好ましい。皮膜厚が5nm未満ではラミネートフィルムの優れた密着性が得られず、500nmを超えると金属材料の有する色調を損ねる可能性が高い。また、下地皮膜の全付着量は炭素として5~500mg/m²の範囲にあることが必要であり、50~200mg/m²の範囲にあることが好ましい。下地皮膜の全付着量が5mg/m²未満では優れた密着性が得られず、500mg/m²を超えると金属材料の有する色調を損ねる可能性が高い。本発明の被覆金属材料の下地皮膜については、さらに、該皮膜が金属材料の表面の90%以上を被覆していなければならない。90%未満の被覆率では加工時にフィルムが剥離しやすい。

【0029】上記炭素付着量、皮膜厚および被覆率の測定方法について以下に説明する。炭素付着量の測定は市販の表面炭素分析装置を用いて測定する。すなわち、まず本発明の被覆金属材料を適当なサイズ(20~50cm²程度)に切り出してサンプルとする。表面炭素分析装置はサンプルを昇温し、表面に存在する炭素を酸化してガス化し、このガスをIR(赤外吸収)で定量する原理となっている。測定条件は表面の炭素を酸化してガス化させる条件であれば良いが、一般に400~500℃で5~10分の条件で測定することが好ましい。皮膜厚および被覆率は市販のXPS(X線光電子分光分析)装置で定量する。XPSとはサンプルを超高真空(10⁻⁵Pa以下)においてX線で励起し、この際に放出される光電子を分析する装置である。この光電子の強度と感度係数より表面に存在する原子の比率を計算することができる。なお、皮膜厚および被覆率の定量計算方法はすでに確立されたものであり、プログラムとして市販されている。

【0030】まず被覆率の測定について説明する。大気にさらされたサンプルは必ず何らかの汚染を受けている。このため、大気中で清浄にしたサンプルでもXPSで分析すると最表面には炭素等の汚染物が検出される。この影響を除去するため、本発明における被覆率の算定に際しては、最表面をアルゴンで若干スパッタリング

(2nm)してから分析を行っている。すなわち、XPS分析装置に併設されている市販のアルゴンスパッタリングガンを用いて表面を2nmスパッタリングして汚染物を除去した後にX線で表面を励起し光電子を分析した。X線で励起した後、ワイドスキャンと呼ばれる分析を行い、まず、表面に存在する原子の定性を行う。本発明において下地皮膜で検出される元素は、通常、炭素、酸素、リン、ケイ素、ジルコニウム、チタン、金属材料(鉄、アルミニウム)が主である。定性にて測定された元素について定量計算を行い、これより金属材料の原子

%であるAを算出する。このAを用いて被覆率を次式(V)により計算する。

$$\text{被覆率} = 100 - A \quad (V)$$

【0031】次に、皮膜厚は上述のアルゴンスパッタリングガンを用いて測定する。皮膜厚が既知(透過電子顕微鏡等で測定)の皮膜厚が異なる幾つかのサンプルについて皮膜厚を測定する。まず、各サンプルについて、アルゴンスパッタリング光電子分析を数回繰り返す。上記被覆率が40%になるまで皮膜が存在したと仮定し、これに要したスパッタリングの積算時間と皮膜厚との間の検量線を作成する。ついで、本発明の被覆金属材料からのサンプルを分析し、被覆率が40%になるまでのスパッタリング積算時間と検量線より皮膜厚を算出する。

【0032】次に、本発明の被覆金属材料の製造方法について説明する。金属材料にフィルムラミネート用下地皮膜を施して本発明の被覆金属材料を製造するに先立ち、まず金属材料表面を清浄にする必要がある。すなわち、工業的に使用される金属材料は圧延油が付着していたり、防錆油等が塗布されていることが多いので、これら除去(脱脂)する必要がある。脱脂方法は特に制限されず、一般的に使用される溶剤脱脂、アルカリ脱脂または酸系脱脂を採用することができる。本発明の被覆金属材料は、すでに述べたごとく、前述したフィルムラミネート用下地皮膜を反応型皮膜として施すことにより製造しても良く、塗布型皮膜として施すことにより製造しても良い。ここで「反応型」とは、すでに述べたごとく、金属材料表面と反応させて、その後、表面に残存する未反応物を水洗で除去する処理方法を意味し、塗布型とは、塗布して水洗なしで乾燥する処理方法を意味する。

【0033】反応型皮膜を形成させる場合の本発明の被覆金属材料の製造は、すでに述べたごとく、上記重合体と水からなり、必要に応じリン酸系化合物および有機ケイ素化合物の少なくとも1種を含有し、pHを2.5~6.5に調整した水系組成物であって、重合体の濃度が0.1g/L以上であり、存在させる場合のリン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度が0.1g/L以上である該水系組成物を金属材料の表面と接触させて該表面と反応させることによりフィルムラミネート用下地皮膜を形成させることにより行うことができる。

【0034】上記において重合体、リン酸系化合物および有機ケイ素化合物としては、本発明の被覆金属材料についての説明で挙げたものと同じものを挙げるができる。pHは好ましくは3.0~5.0に調整する。pHが2.5未満であると皮膜の形成が充分でなく、6.5を超えると水系組成物の安定性に問題が生じる。このpHの調整は、必要に応じ、リン酸、縮合リン酸、フッ化水素酸等の等の酸、特に鉱酸、水酸化ナトリウム等に

より行うことができる。これらの酸はエッチング剤として作用する。また、このエッチング効率を高めるために、すなわちエッチング助剤として過酸化水素等を用いることができる。重合体の濃度は0.1g/L以上であることが必要であり、0.1~10g/Lであることが好ましく、0.3~3g/Lであることがさらに好ましい。重合体の濃度が0.1g/L未満であると皮膜の形成が充分でなく、10g/Lを超えるとコストが高くなる。リン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度は0.1g/L以上であることが必要であり、0.1~30g/Lであることが好ましく、0.3~1g/Lであることがさらに好ましい。リン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度が0.1g/L未満であると反応性が不十分であり、30g/Lを超えるとコストが高くなる。

【0035】上記水系組成物と金属材料の表面との接触は、特に制限されないが、通常、該水系組成物を金属材料表面にスプレーするかまたは金属材料を該水系組成物に浸漬することにより行うことができる。上記処理時の該水系組成物の温度は、特に制限されないが、通常40~60℃であることが好ましい。スプレーの場合、スプレー後1~30秒程度放置するのが好ましく、浸漬の場合、浸漬時間は1~30秒程度であることが好ましい。この接触によって金属材料表面がエッチングされ部分的な界面pHの上昇が起こり、この際に重合体が表面に析出し、これを被覆する。反応型皮膜を形成させる場合には、接触処理後、通常、未反応物を水洗により除去する。ついで、通常、塗膜の乾燥を行うが、この際の乾燥温度は、特に制限されないが、通常60~200℃であることが好ましく、乾燥は通常熱風乾燥により行う。乾燥皮膜について、皮膜厚、皮膜付着量および被覆率、さらにはリン酸系化合物の付着量および有機ケイ素化合物の付着量は、本発明の被覆金属材料について説明した範囲になるように調整するが、この調整は、上記水系組成物中の重合体の濃度、エッチング剤の濃度、リン酸系化合物の濃度、有機ケイ素化合物の濃度、処理温度、処理時間等を調整することにより行うことができる。反応型皮膜を形成させることによるメリットは、薄い皮膜厚で高い被覆率が達成され、かつ、均一性の良い皮膜が得られることである。

【0036】塗布型皮膜を形成させる場合の本発明の被覆金属材料の製造は、すでに述べたごとく、上記重合体と水からなり、必要に応じリン酸系化合物および有機ケイ素化合物の少なくとも1種を含有する水系組成物であって、重合体の濃度が0.01g/L以上であり、リン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度が0.01g/L以上である該水系組成物を金属材料の表面に塗布して該表面にフィルムラミネート用下地皮膜を形成させ、ついで該表面を乾燥することにより行うことができる。

【0037】上記において重合体、リン酸系化合物および有機ケイ素化合物としては、本発明の被覆金属材料についての説明で挙げたものと同じものを挙げるができる。重合体の濃度は0.01g/L以上であることが必要であり、0.01~10g/Lであることが好ましく、0.1~2g/Lであることがさらに好ましい。重合体の濃度が0.01g/L未満であると充分な付着量が得られず、10g/Lを超えるとコストが高くなる。リン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度は0.01g/L以上であることが必要であり、0.01~30g/Lであることが好ましく、0.05~3g/Lであることがさらに好ましい。リン酸系化合物および有機ケイ素化合物の少なくとも1種の濃度が0.01g/L未満であると充分な付着量が得られず、30g/Lを超えるとコストが高くなる。上記水系組成物のpHは、反応型皮膜を形成させる場合と異なり、任意的であり特に制限されないが、通常3~6程度であることが適当である。

【0038】上記水系組成物の金属材料表面への塗布は、特に制限されないが、通常、該水系組成物を金属材料表面にロールコート等にて塗布することにより行うことができる。塗布時の該水系組成物の温度は、特に制限されないが、通常15~35℃であることが好ましい。ついで、通常、塗膜の乾燥を行うが、この際の乾燥温度は、特に制限されないが、通常80~200℃であることが好ましく、乾燥は通常熱風乾燥により行う。乾燥皮膜について、皮膜厚、皮膜付着量および被覆率、さらにはリン酸系化合物の付着量および有機ケイ素化合物の付着量は、本発明の被覆金属材料について説明した範囲になるように調整するが、この調整は、上記水系組成物中の重合体の濃度、リン酸系化合物の濃度、有機ケイ素化合物の濃度、塗布温度等を調整することにより行うことができる。塗布型皮膜を形成させることによるメリットは、連続工程の一環として処理を行えることである。すなわち、連続工程でフィルムラミネートを行う場合の、前処理として、塗布型皮膜形成を行える点である。

【0039】上記のようにして調製した、金属材料の表面にフィルムラミネート用下地皮膜を形成させた、本発明の被覆金属材料にフィルムをラミネートする場合、その方法は従来のクロム系の下地皮膜が施された被覆金属材料にフィルムをラミネートする場合と同様で良い。ラミネートするフィルムは特に制限されず、従来の技術の項で述べたような従来使用されているラミネート用フィルムを用いることができる。具体的には例えばポリエステルフィルム、特にテレフタル酸ビニルを主体とするフィルム、ポリエチレンフィルム、ポリカーボネートフィルム等の熱可塑性樹脂のフィルムが挙げられる。ラミネートするフィルムの形状は特に制限されないが、通常板状、シート状等のものを使用する。かかるフィルムのラミネート方法についても特に制限はないが、通常フィル

ムを加熱軟化させてラミネートする。この際接着剤の使用は通常不要であるが、使用しても構わない。

【0040】

【実施例】以下に本発明の下地皮膜に関し、幾つかの実施例を挙げ、その有用性を比較例と対比して示す。

【金属材料】

1 アルミニウム合金板

市販のアルミニウム-マンガン合金板 (JIS A3004 板厚: 0.3mm 板寸法: 200×300mm) を、市販の酸性洗浄剤 (パルクリーン500: 日本パーカライジング株式会社製) の8%水溶液を75℃で20秒スプレーすることにより洗浄し、ついで水洗して表面を清浄にした。

2 鋼板

市販の冷延鋼板 (JIS SPCC 板厚: 0.3mm 板寸法: 200×300mm) を、市販の洗浄剤 (ファインクリーナー4328: 日本パーカライジング株式会社製) の2%水溶液を60℃で20秒スプレーすることにより洗浄し、ついで水洗して表面を清浄にした。

【0041】 [被覆金属材料の製造] アルミニウム合金板または鋼板を下記実施例または比較例にしたがって被覆処理し、反応型下地皮膜または塗布型下地皮膜を形成させた。

【0042】 [炭素付着量測定方法] 上記下地皮膜の炭素付着量 (mg/m^2) を市販の表面炭素分析装置 (LECO製) を用いて測定した。サンプルサイズは32 cm^2 で測定条件は400℃-8分とした。

【被覆率および皮膜厚】 上記下地皮膜の状態を市販のXPS (X線光電子分光分析) 装置 (島津製作所製) を用いて分析した。励起X線としてMgを用い、条件は8kV-30mAとした。試料のサイズは $\phi 5\text{mm}$ とした。最表面を2nmスパッタリングして、定性分析を行った。この際検出された元素を定量計算し、前述の式

(V) に従い、被覆率を算出した。また、XPS装置に市販のアルゴンスパッタリングガン (島津製作所製) を併設し、スパッタリングにて皮膜を破壊除去した。スパッタリングの条件は600V-50mAとした。この際

水系組成物 1

下記水溶性重合体 1 固形分

pH 6.0 (リン酸で調整)

水溶性重合体 1

X^1 が、式 (I) で表されるそれぞれの構成単位において独立に、水素原子または $Z^{1A} = -\text{CH}_2\text{N}(\text{CH}_3)_2$ であり、 $Y^1 = Y^2 =$ 水素原子であり、 Z^{1A} 基の導入率がベンゼン環 1 個あたり 0.5 個である式 (I) で表され

水系組成物 2

下記水溶性重合体 2 固形分

pH 6.0 (リン酸で調整)

水溶性重合体 2

X^1 が、式 (I) で表されるそれぞれの構成単位におい

のスパッタリング時間より前述の方法にしたがって皮膜厚 (nm) を求めた。

【0043】 [フィルムラミネートと成形] 上記被覆金属材料にポリエステル系フィルム (膜厚 $30\mu\text{m}$) を180℃でラミネートした。その後、この金属材料を $\phi 140\text{mm}$ に打ち抜き、これを絞りカップを作製した。ついでこのカップを再度絞り、さらにしごき加工を3枚のダイで行い、絞りしごき缶を作製した。

【0044】 [フィルムラミネートした被覆金属材料の性能評価]

1 成形性

絞りしごき加工した際に、破断した場合を「×」、破断しないもののキズが入った場合を「△」、破断はもちろんキズもない場合を「○」として評価した。

2 耐食性

絞りしごき加工により成形した缶体を用い、市販のエナメルレーター (Peco社製) でもれ電流を測定した。測定液は0.5%の食塩水を用い、6.3Vで4秒後の電流値を測定した。電流値は低い方が好ましい。0.3mA未満の場合を「○」、0.3mA以上1.0mA未満の場合を「△」、1.0mA以上の場合を「×」として評価した。

3 密着性

絞りしごき加工により成形した缶体を市販の滅菌器でレトルト (= 加圧蒸気中で加温) した。条件は121℃-30分とした。レトルト処理後のフィルムの密着状態より密着性を評価した。素地との剥離が全くない場合を「○」、一部剥離の場合を「△」、全面剥離の場合を「×」として評価した。

4 環境安全性

下地皮膜を形成するに際して、人体に有害な物質である6価クロムを使用する場合を「×」、使用しない場合を「○」として評価した。

【0045】 実施例 1

上記アルミニウム合金板に下記水系組成物 1 を塗布し、ついで80℃で塗膜を乾燥して塗布型下地皮膜を形成させた。

2.0 g/L

る重合体であって、平均分子量3000のもの

【0046】 実施例 2

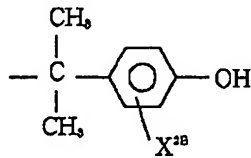
上記アルミニウム合金板に下記水系組成物 2 を塗布し、ついで80℃で塗膜を乾燥して塗布型下地皮膜を形成させた。

0.5 g/L

て独立に、水素原子または $Z^{1B} = -\text{CH}_2\text{N}(\text{CH}_3)_2$ であり、 Y^1 が式

【0047】

【化9】



【0048】(式中、 X^{2B} は、式(1)で表されるそれぞれの構成単位において独立に、水素原子または $Z^{2B} =$

水系組成物3

HF

0.05 g/L

 H_3PO_4

2.0 g/L

 $Na_4P_2O_7 \cdot 10H_2O$

2.0 g/L

下記水溶性重合体3固形分

5.0 g/L

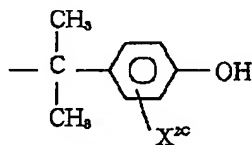
pH 4.0 (水酸化ナトリウムで調整)

水溶性重合体3

X^1 が、式(1)で表されるそれぞれの構成単位において独立に、水素原子または $Z^{1C} = -CH_2N(CH_2CH_2OH)_2$ であり、 Y^1 が式

【0050】

【化10】



水系組成物4

HF

0.05 g/L

 H_2O_2

1.0 g/L

 H_3PO_4

2.0 g/L

 $Na_4P_2O_7 \cdot 10H_2O$

2.0 g/L

下記水溶性重合体4固形分

5.0 g/L

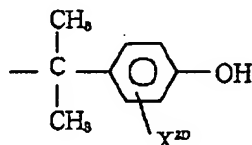
pH 3.5 (水酸化ナトリウムで調整)

水溶性重合体4

X^1 が、式(1)で表されるそれぞれの構成単位において独立に、水素原子または $Z^{1D} = -CH_2N(CH_2CH_2CH_2OH)(CH_3)$ であり、 Y^1 が式

【0053】

【化11】



水系組成物5

水溶性重合体1固形分

2.0 g/L

 H_2ZrF_6

0.1 g/L

 H_3PO_4

0.1 g/L

pH 6.0 (アンモニア水で調整)

【0056】実施例3

$-CH_2N(CH_3)_2$ である)で表される基であり、 Y^2 が水素原子であり、 Z^{1B} 基+ Z^{2B} 基の導入率がベンゼン環1個あたり1.0個である式(1)で表される重合体であって、平均分子量15000のもの

【0049】実施例3

上記アルミニウム合金板に下記水系組成物3を組成物温度50℃で20秒スプレーし、表面を水洗-脱イオン水洗し、ついで80℃で塗膜を乾燥して反応型下地皮膜を形成させた。

【0051】(式中、 X^{2C} は、式(1)で表されるそれぞれの構成単位において独立に、水素原子または $Z^{2C} = -CH_2N(CH_2CH_2OH)_2$ である)で表される基であり、 Y^2 が水素原子であり、 Z^{1C} 基+ Z^{2C} 基の導入率がベンゼン環1個あたり0.75個である式(1)で表される重合体であって、平均分子量5000のもの

【0052】実施例4

上記アルミニウム合金板に下記水系組成物4を組成物温度60℃で4秒浸漬し、表面を水洗-脱イオン水洗し、ついで80℃で塗膜を乾燥して反応型下地皮膜を形成させた。

【0054】(式中、 X^{2D} は、式(1)で表されるそれぞれの構成単位において独立に、水素原子または $Z^{2D} = -CH_2N(CH_2CH_2CH_2OH)(CH_3)$ である)で表される基であり、 Y^2 が水素原子であり、 Z^{1D} 基+ Z^{2D} 基の導入率がベンゼン環1個あたり0.50個である式(1)で表される重合体であって、平均分子量7500のもの

【0055】実施例5

上記鋼板に下記水系組成物5を塗布して塗布型下地皮膜を形成させ、ついで80℃で塗膜を乾燥した。

50 上記鋼板に下記水系組成物6を塗布し、ついで80℃で

塗膜を乾燥して塗布型下地皮膜を形成させた。

水系組成物6

| | |
|-----------------------|----------|
| 水溶性重合体3固形分 | 2.0 g/L |
| H_2ZrF_6 | 0.1 g/L |
| H_3PO_4 | 0.1 g/L |
| γ-グリシドキシプロピルトリメトキシシラン | 0.05 g/L |
| pH 6.0 (アンモニア水で調整) | |

【0057】実施例7

上記鋼板に下記水系組成物7を組成物温度60℃で10

秒浸漬し、表面を水洗-脱イオン水洗し、ついで80℃で塗膜を乾燥して反応型下地皮膜を形成させた。

水系組成物7

| | |
|---------------------------|----------|
| HF | 0.10 g/L |
| H_2O_2 | 2.0 g/L |
| H_3PO_4 | 2.0 g/L |
| $Na_4P_2O_7 \cdot 10H_2O$ | 2.0 g/L |
| 下記水溶性重合体3固形分 | 5.0 g/L |
| pH 4.0 (水酸化ナトリウムで調整) | |

【0058】比較例1

上記アルミニウム合金板に、市販のリン酸クロメート化成剤（アルクロムK702：日本パーカラライジング株式会社製）の4%水溶液を該水溶液温度50℃で10秒スプレーし、表面を水洗-脱イオン水洗し、ついで80℃で塗膜を乾燥して下地皮膜を形成させた。

剤（アロジンN-405：日本パーカラライジング株式会社製）の2%水溶液を該水溶液温度40℃で10秒スプレーし、表面を水洗-脱イオン水洗し、ついで80℃で塗膜を乾燥して下地皮膜を形成させた。

【0059】比較例2

上記アルミニウム合金板に、市販のジルコニウム系化成

【0060】比較例3

上記鋼板に下記水系組成物8を塗布し、ついで80℃で塗膜を乾燥して下地皮膜を形成させた。

水系組成物8

| | |
|-----------------------|----------|
| H_2ZrF_6 | 0.1 g/L |
| H_4PO_4 | 0.1 g/L |
| γ-グリシドキシプロピルトリメトキシシラン | 0.05 g/L |
| pH 6.0 (アンモニア水で調整) | |

【0061】比較例4

市販のTFS（クロム系の皮膜処理が施されている）を用いた。

【0062】上記実施例1～7および比較例1～4において製造した被覆金属材料の下地皮膜の皮膜厚、炭素付着量、被覆率を表1に示す。また、該被覆金属材料の性能の評価結果も表1に併せて示す。表1の結果から明らかなように、実施例1～7の本発明の被覆金属材料は成形性、耐食性、密着性および環境安全性のすべてに優れ

30 ている。他方、リン酸クロメート皮膜を施した比較例1の被覆金属材料、ジルコニウム系皮膜を施した比較例2の被覆金属材料、本発明で使用する重合体を含まない皮膜を施した比較例3の被覆金属材料およびTFSは、成形性、耐食性、密着性および環境安全性をすべてを満足することはできない。

【0063】

【表1】

表1. 評価結果

| | 処理 | | 下地皮膜 | | | | | 性能評価 | | | |
|------|-----|----|------------|---------------------------|----------|---------------------------|----------------------------|------|--------------------|--------------------|-------|
| | 素材 | 方法 | 皮膜厚さ μm | C付着量 mg/m ² | 被覆率 % | P付着量 mg/m ² | Si付着量 mg/m ² | 成形性 | 耐食性 | 密着性 | 環境安全性 |
| 実施例1 | アルミ | 塗布 | 200 | 200 | 96 | 5 | 0 | ○ | ○ | ○ | ○ |
| 実施例2 | アルミ | 塗布 | 100 | 100 | 90 | 5 | 0 | ○ | ○ | ○ | ○ |
| 実施例3 | アルミ | 反応 | 20 | 20 | 95 | 3 | 0 | ○ | ○ | ○ | ○ |
| 実施例4 | アルミ | 反応 | 30 | 30 | 97 | 3 | 0 | ○ | ○ | ○ | ○ |
| 実施例5 | 銅板 | 塗布 | 250 | 250 | 95 | 10 | 0 | ○ | ○ | ○ | ○ |
| 実施例6 | 銅板 | 塗布 | 250 | 250 | 95 | 5 | 2 | ○ | ○ | ○ | ○ |
| 実施例7 | 銅板 | 反応 | 15 | 15 | 90 | 2 | 0 | ○ | ○ | ○ | ○ |
| 比較例1 | アルミ | 反応 | 50 | 2 ^{※1} | 85 | 10 | 0 | △ | × | × | × |
| 比較例2 | アルミ | 反応 | 25 | 2 ^{※1} | 85 | 5 | 0 | × | 測定不能 ^{※2} | 測定不能 ^{※2} | ○ |
| 比較例3 | 銅板 | 塗布 | 100 | 2 ^{※1} | 80 | 4 | 1 | × | 測定不能 ^{※2} | 測定不能 ^{※2} | ○ |
| 比較例4 | TFS | なし | - | 2 ^{※1} | - | 0 | 0 | ○ | ○ | ○ | × |

*1: 大気からの表面汚染に起因し検出されたものである

*2: 缶に成形できなかった。耐食性、密着性は缶に成形できたものについて試験するため、測定不能と記した。

【0064】

【発明の効果】本発明の被覆金属材料は成形性、耐食

性、密着性及び環境安全性のすべてに優れている。